

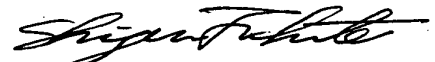


DECLARATION

I, Shigeru FUCHITA, do solemnly and sincerely declare that I understand the Japanese language and the English language well, and that the attached English version is a full, true and faithful translation made by me of Japanese Application for Patent No. 10-50541.

I make this solemn declaration conscientiously believing the same to be true.

November 22, 2002


Shigeru FUCHITA

[Document] Application for Patent

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[To:] Director-General of the Patent Office

[Title of the invention]

Olefin polymerization catalysts, processes for olefin polymerization, and α -olefin/conjugated diene copolymer

[Number of Claims] 8

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[List of the Appended Documents]

Description	1
Drawing	1
Abstract	1
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[Necessity or not of group] Necessity

[Document] Specification

[Title of the invention]

Olefin polymerization catalysts, process for olefin polymerization, and α -olefin/conjugated diene copolymers

5 [What is claimed is:]

1. An olefin polymerization catalyst comprising:

(A) a transition metal compound represented by the following formula (I), and

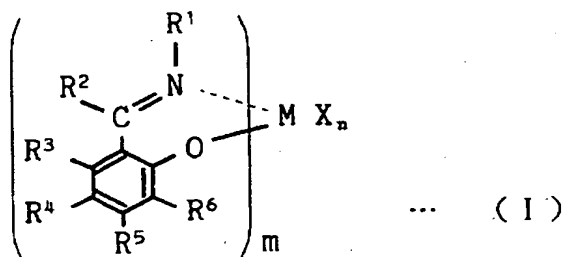
(B) at least one compound selected from:

10 (B-1) an organometallic compound,

(B-2) an organoaluminum oxy-compound, and

(B-3) a compound which reacts with the transition metal compound (A) to form an ion pair:

15



20 wherein M is a transition metal atom of Group 3 to Group 11 of the periodic table,

m is an integer of 1 to 3,

R¹ to R⁶ may be the same or different, and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a

heterocyclic compound residue, a hydrocarbon-substituted silyl group, a hydrocarbon-substituted siloxy group, an alkoxy group, a thioalkoxy group, an aryloxy group, a thioaryloxy group, an acyl group, an ester group, a thioester group, an amido group, an imido group, an amino group, an imino group, a sulfonester group, a sulfonamido group, a cyano group, a nitro group or a hydroxyl group, and two or more of them may be bonded to each other to form a ring,

when m is 2 or more, two of the groups R^1 to R^6 may be bonded to each other,

n is a number satisfying a valence of M, and

X is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group or a silicon-containing group, and when n is 2 or more, plural groups X may be the same or different and may be bonded to each other to form a ring.

2. The olefin polymerization catalyst as claimed in claim 1, wherein the transition metal compound (A) is a compound in which R^6 in the formula (I) is a halogen atom, a hydrocarbon group, a heterocyclic compound residue, a hydrocarbon-substituted silyl group, a hydrocarbon-substituted siloxy group, an alkoxy group, an thioalkoxy group, an aryloxy group,

a thioaryloxy group, an acyl group, an ester group, a thioester group, an amido group, an imido group, an amino group, an imino group, a sulfonester group, a sulfonamido group, a cyano group, a nitro group or a hydroxyl group.

5

3. The olefin polymerization catalyst comprising a fine particle carrier (C) in addition to the transition metal compound (A) and at least one compound (B) selected from the organometallic compound (B-1), the organoaluminum
10 oxy-compound (B-2) and the ionizing ionic compound (B-3).

4. A process for olefin polymerization, comprising polymerizing or copolymerizing an olefin in the presence of the olefin polymerization catalyst as claimed in any one of
15 claims 1 to 3.

5. An α -olefin/conjugated diene copolymer having a molecular weight distribution (Mw/Mn) of not more than 3.5, a content of constituent units derived from an α -olefin in the
20 range of 1 to 99.9 % by mol and a content of constituent units derived from a conjugated diene in the range of 99 to 0.1 % by mol, in which the polymer chain contains 1,2-cyclopentane skeleton derived from the conjugated diene in an amount of not more than 1 % by mol.

6. The α -olefin/conjugated diene copolymer as claimed in claim 5, wherein the polymer chain does not substantially contain the 1,2-cyclopentane skeleton derived from the conjugated diene.

5

7. The α -olefin/conjugated diene copolymer as claimed in claim 5 or 6, wherein the content of the constituent units derived from the α -olefin is in the range of 50 to 99.9 % by mol and the content of the constituent units derived from
10 the conjugated diene is in the range of 50 to 0.1 % by mol.

8. The α -olefin/conjugated diene copolymer as claimed in any one of claims 5 to 7, wherein the α -olefin is ethylene or propylene and the conjugated diene is butadiene
15 or isoprene.

[Detailed description of the invention]

[0001]

[Field of the invention]

20 The present invention relates to novel olefin polymerization catalysts and processes for olefin polymerization using the olefin polymerization catalysts.

[0002]

It is also an object of the present invention to provide

α -olefin/conjugated diene copolymers which have narrow molecular weight distribution and are favorably used as rubbers.

[0003]

[Background of the invention]

5 As olefin polymerization catalysts, so-called "Kaminsky catalysts" are well known. The Kaminsky catalysts have extremely high polymerization activities, and by the use of them, polymers of narrow molecular weight distribution can be obtained. As the transition metal compounds used for the Kaminsky catalysts, 10 for example, bis(cyclopentadienyl)zirconium dichloride (see: Japanese Patent Laid-Open Publication No. 19309/1983) and ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride (see: Japanese Patent Laid-Open Publication No. 130314/1986) are known. It is also known that the olefin polymerization 15 activities or the properties of the resulting polyolefins greatly vary when different transition metal compounds are used in the polymerization. Further, transition metal compounds having a ligand of diimine structure have been recently proposed as novel olefin polymerization catalysts (see: 20 International Patent Publication No. 9623010).

[0004]

Polyolefins generally have excellent mechanical properties, and therefore they are used in various fields such as molded products of all sorts. However, with variation of

requirements for the polyolefins, polyolefins of various properties have been desired in recent years. Moreover, increase of productivity has been also desired.

[0005]

5 Under such circumstances, there has been desired development of olefin polymerization catalysts having excellent olefin polymerization activities and capable of producing polyolefins of excellent properties.

[0006]

10 Under such circumstances, there has been desired development of olefin polymerization catalysts having excellent olefin polymerization activities and capable of producing polyolefins of excellent properties.

[0006]

15 It is well known that copolymerization of several kinds of α -olefins and non-conjugated dienes proceeds when Ziegler-Natta polymerization catalysts are used. Since the copolymers obtained are useful as rubbers, copolymers of various types have been produced. However, the non-conjugated
20 dienes used in the copolymerization are generally expensive and have low reactivity. Therefore, diene components which are inexpensive and have high reactivity are desired.

[0007]

Examples of such diene components include conjugated

dienes such as 1,3-butadiene and isoprene. Though these conjugated dienes are more inexpensive and have higher reactivity as compared with the conventional non-conjugated dienes, they have problem such that the activities are markedly
5 lowered or only ununiform copolymers of wide composition distribution or wide molecular weight distribution are obtained if the copolymerization is conducted by the use of the conventional Ziegler-Natta polymerization catalysts. In case of a Ziegler-Natta catalyst system using a vanadium compound,
10 the polymerization activities are extremely low, though relatively uniform copolymers are obtainable. In the circumstances, copolymerization of ethylene and butadiene using metallocene catalysts which have been studied actively and known to exhibit high polymerization activities has been investigated (National
15 Publication of International Patent No. 501633/1989).

[0008]

In the above case, however, it has been reported that from the diene unit and ethylene incorporated into the polymer form together cyclopentane skeleton in the polymer chain, and
20 that the proportion of the cyclopentane skeleton becomes not less than 50 % of all the diene units. The conversion of double bonds of the diene unit into the cyclopentane skeleton is very disadvantageous in the procedure of "vulcanization" required to use the copolymers as rubbers. Further, the cyclopentane skeleton

is an unfavorable skeleton because it functions to increase glass transition temperature of the copolymers and is detrimental to the low-temperature properties of the rubbers.

[0009]

5 Under these circumstances, there has been eagerly desired development of copolymers of α -olefins and conjugated dienes, which have narrow molecular weight distribution and uniform composition and contain almost no cyclopentane skeleton in their polymer chains.

10 [0010]

[Object of the invention]

It is an object of the present invention to provide an olefin polymerization catalyst having excellent olefin polymerization activities and a process for olefin

15 polymerization using the catalyst.

[0011]

It is a further object of the present invention to provide an α -olefin/conjugated diene copolymer containing almost no cyclopentane skeleton in its polymer chain.

20 [0012]

[Summary of the invention]

The olefin polymerization catalyst according to the invention comprises:

(A) a transition metal compound represented by the

following formula (I), and

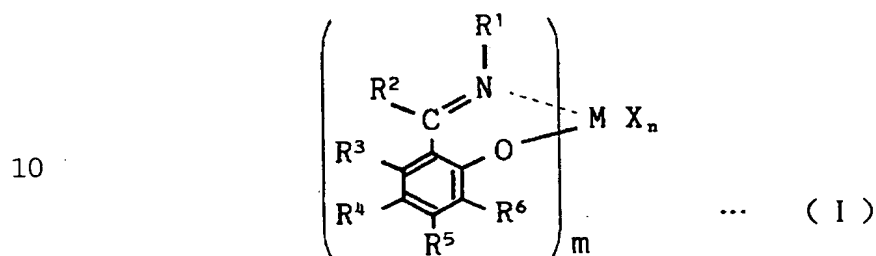
(B) at least one compound selected from:

(B-1) an organometallic compound,

(B-2) an organoaluminum oxy-compound, and

5 (B-3) a compound which reacts with the transition metal compound to form an ion pair:

[0013]



[0014]

wherein M is a transition metal atom of Group 3 to Group 11
15 of the periodic table,

m is an integer of 1 to 3,

R¹ to R⁶ may be the same or different, and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residue, a hydrocarbon-substituted
20 silyl group, a hydrocarbon-substituted siloxy group, an alkoxy group, a thioalkoxy group, an aryloxy group, a thioaryloxy group, an acyl group, an ester group, a thioester group, an amido group, an imido group, an amino group, an imino group, a sulfonester group, a sulfonamido group, a cyano group, a nitro

group or a hydroxyl group, and two or more of them may be bonded to each other to form a ring,

when m is 2 or more, two of the groups R^1 to R^6 may be bonded to each other,

5 n is a number satisfying a valence of M , and

X is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group or a silicon-containing group, and
10 when n is 2 or more, plural groups X may be the same or different and may be bonded to each other to form a ring.

 In the present invention, the transition metal compound (A) is preferred that R^6 in the formula (I) is a halogen atom, a hydrocarbon group, a heterocyclic compound residue, a hydrocarbon-substituted silyl group, a hydrocarbon-substituted
15 siloxy group, an alkoxy group, an thioalkoxy group, an aryloxy group, a thioaryloxy group, an acyl group, an ester group, a thioester group, an amido group, an imido group, an amino group, an imino group, a sulfonester group, a sulfonamido group, a
20 cyano group, a nitro group or a hydroxyl group.

[0015]

 Further, the olefin polymerization catalyst according to the invention may comprise a fine particle carrier (C) in addition to the transition metal compound (A) and at least one

compound (B) selected from the organometallic compound (B-1), the organoaluminum oxy-compound (B-2) and the ionizing ionic compound (B-3).

[0016]

5 The process for olefin polymerization according to the invention comprises polymerizing or copolymerizing an olefin in the presence of the olefin polymerization catalyst as described above.

10 The α -olefin/conjugated diene copolymer is an α -olefin/conjugated diene copolymer having a molecular weight distribution (Mw/Mn) of not more than 3.5, a content of constituent units derived from an α -olefin in the range of 1 to 99.9 % by mol and a content of constituent units derived from a conjugated diene in the range of 99 to 0.1 % by mol,
15 in which the polymer chain contains 1,2-cyclopentane skeleton derived from the conjugated diene in an amount of not more than 1 % by mol, and preferably the polymer chain does not substantially contain the 1,2-cyclopentane skeleton.

[0017]

20 Also, in the α -olefin/conjugated diene copolymer according to the invention, it is preferred that the content of the constituent units derived from the α -olefin is in the range of 50 to 99.9 % by mol and the content of the constituent units derived from the conjugated diene is in the range of 50

to 0.1 % by mol.

[0018]

Further, in the α -olefin/conjugated diene copolymer according to the invention, it is preferred that the α -olefin
5 is ethylene or propylene and the conjugated diene is butadiene or isoprene.

[0019]

[Specific description of the invention]

The olefin polymerization catalyst of the present
10 invention and the process for olefin polymerization using the catalyst are described specifically hereinafter.

[0020]

The meaning of the term "polymerization" used herein is not limited to "homopolymerization" but may comprehend "copolymerization".
15 Also, the meaning of the term "polymer" used herein is not limited to "homopolymer" but may comprehend "copolymer".

[0021]

The olefin polymerization catalyst of the invention is formed from:

20 (A) a transition metal compound represented by the following formula (I), and

(B) at least one compound selected from:

(B-1) an organometallic compound,

(B-2) an organoaluminum oxy-compound, and

(B-3) a compound which reacts with the transition metal compound to form an ion pair.

[0022]

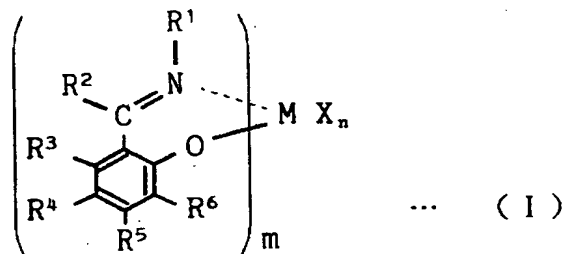
First, the catalyst components for forming the olefin
5 polymerization catalyst of the invention are described.

(A) Transition metal compound

The transition metal compound (A) for use in the invention is a compound represented by the following formula (I).

[0023]

10



15 [0024]

In the above formula (I), M is a transition metal atom of Group 3 to Group 11 of the periodic table, preferably Group 3 to Group 5 and Group 9, for example, preferably scandium, titanium, zirconium, hafnium, vanadium, niobium, tantalum,
20 palladium, nickel, cobalt and rhodium, more preferably titanium, zirconium, hafnium, cobalt and rhodium, particularly preferably titanium, zirconium and hafnium.

[0025]

m is an integer of 1 to 3.

R^1 to R^6 may be the same or different, and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residues, a hydrocarbon-substituted silyl group, a hydrocarbon-substituted siloxy group, an alkoxy group, an thioalkoxy group, an aryloxy group, an thioaryloxy group, a thioester group, an ester group, an acyl group, an amido group, an imido group, an amino group, an imino group, a sulfonester group, a sulfonamido group, a cyano group, a nitro group or a hydroxyl group. Of these, particularly preferable is a hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group, an alkoxy group, an aryloxy group, an ester group, an amido group, an amino group, a sulfonamido group, a cyano group or a nitro group.

[0026]

15 The halogen atom is fluorine, chlorine, bromine or iodine.

Examples of the hydrocarbon groups include straight-chain or branched alkyl groups of 1 to 20 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl and hexyl; straight-chain or branched alkenyl groups of 2 to 20 carbon atoms, such as vinyl, allyl and isopropenyl; straight-chain or branched alkynyl groups of 2 to 20 carbon atoms, such as ethynyl and propargyl; cyclic saturated hydrocarbon groups of 3 to 20 carbon atoms, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and

adamantyl; aryl groups of 6 to 20 carbon atoms, such as phenyl, benzyl, naphthyl, biphenyl and triphenyl; cyclic unsaturated hydrocarbon groups of 5 to 20 carbon atoms, such as cyclopentadienyl, indenyl and fluorenyl; and these groups which are substituted
5 with substituents such as alkyl groups of 1 to 20 carbon atoms, halogenated alkyl groups of 1 to 20 carbon atoms, aryl groups of 6 to 20 carbon atoms, alkoxy groups, aryloxy groups, halogen, cyano, nitro and hydroxyl. Of these, particularly preferable are straight-chain or branched alkyl groups of 1 to 20 carbon
10 atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl and hexyl; aryl groups of 6 to 20 carbon atoms, such as phenyl and naphthyl; and these aryl groups which are substituted with 1 to 5 substituents such as alkyl groups of 1 to 20 carbon atoms, aryl groups of 6 to
15 20 carbon atoms, alkoxy groups and aryloxy groups.

[0027]

Examples of the heterocyclic residues include residues of nitrogen-containing compounds (e.g., pyrrole, pyridine, pyrimidine, quinoline and triazine), oxygen-containing
20 compounds (e.g., furan and pyran) and sulfur-containing compounds (e.g., thiophene), and these heterocyclic residues which are substituted with substituents such as alkyl groups of 1 to 20 carbon atoms and alkoxy groups.

[0028]

Examples of the hydrocarbon-substituted silyl groups include methylsilyl, dimethylsilyl, trimethylsilyl, ethylsilyl, diethylsilyl, triethylsilyl, diphenylmethylsilyl, triphenylsilyl, dimethylphenylsilyl, dimethyl-t-butylsilyl and

5 dimethyl(pentafluorophenyl)silyl. Of these, particularly preferable are methylsilyl, dimethylsilyl, trimethylsilyl, ethylsilyl, diethylsilyl, triethylsilyl and triphenylsilyl.

[0029]

Examples of the hydrocarbon-substituted siloxy groups

10 include trimethylsiloxo.

Examples of the alkoxy groups include methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy and tert-butoxy.

[0030]

Examples of the thioalkoxy groups include methylthio and

15 ethylthio.

Examples of the aryloxy groups include phenoxy, 2,6-dimethylphenoxy and 2,4,6-trimethylphenoxy.

[0031]

Examples of the thioaryloxy groups include thiophenyl,

20 methylthiophenyl and thionaphthyl.

Examples of the acyl groups include formyl, acetyl, benzoyl, p-chlorobenzoyl and p-methoxybenzoyl.

[0032]

Examples of the ester groups include acetyloxy, benzoyloxy,

methoxycarbonyl, phenoxycarbonyl and p-chlorophenoxycarbonyl.

[0033]

Examples of the thioester groups include acetylthio, benzoylthio and phenylthiocarbonyl.

5 Examples of the amido groups include acetamido, N-methylacetamido and N-methylbenzamido.

[0034]

Examples of the imido groups include acetimido and benzimido.

10 Examples of the amino groups include dimethylamino, ethylmethylamino and diphenylamino.

[0035]

Examples of the imino groups include methylimino, ethylimino, propylimino, butylimino and phenylimino.

15 Examples of the sulfonester groups include methylsulfonato, ethylsulfonato and phenylsulfonato.

[0036]

Examples of the sulfonamido groups include phenylsulfonamido, N-methylsulfonamido and N-methyl-p-toluenesulfonamido.

20 R^6 is preferably a substituent other than hydrogen. That is, R^6 is preferably a halogen atom, a hydrocarbon group, a heterocyclic compound residues, a hydrocarbon-substituted silyl group, a hydrocarbon-substituted siloxy group, an alkoxy group, an thioalkoxy group, an aryloxy group, an thioaryloxy group, an acyl group, an ester group, a thioester group, an

amido group, an amino group, an amino group, an imino group, a sulfonester group, a sulfonamido group, a cyano group, a nitro group or a hydroxyl group.

[0037]

5 Preferred examples of the hydrocarbon groups as R^6 include straight-chain or branched alkyl groups of 1 to 20 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl and hexyl; cyclic saturated hydrocarbon groups of 3 to 20 carbon atoms,
10 such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and adamantyl; aryl groups of 6 to 20 carbon atoms, such as phenyl, benzyl, naphthyl, biphenyl and triphenyl; and these groups which are substituted with substituents such as alkyl groups of 1 to 20 carbon atoms, halogenated alkyl groups of 1 to 20
15 carbon atoms, aryl groups of 6 to 20 carbon atoms, alkoxy groups, aryloxy groups, halogen, cyano, nitro and hydroxyl.

[0038]

Preferred examples of the hydrocarbon-substituted silyl groups as R^6 include methylsilyl, dimethylsilyl, trimethylsilyl, ethylsilyl, diethylsilyl, triethylsilyl, diphenylmethylsilyl,
20 triphenylsilyl, dimethylphenylsilyl, dimethyl-t-butylsilyl and dimethyl(pentafluorophenyl)silyl.

[0039]

In the present invention, R^6 is preferably selected from

branched alkyl groups of 3 to 20 carbon atoms, such as isopropyl, isobutyl, sec-butyl and tert-butyl, these alkyl groups which are substituted with aryl groups of 6 to 20 carbon atoms (e.g., cumyl), and cyclic saturated hydrocarbon groups of 3 to 20 carbon atoms, such as adamantyl, cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. Also, preferable R^6 is a hydrocarbon-substituted silyl group.

[0040]

Two or more groups R^1 to R^6 , preferably adjacent groups, may be bonded to each other to form an aliphatic ring, an aromatic ring or a hydrocarbon ring containing a hetero atom such as a nitrogen atom, and these rings may further have a substituent.

[0041]

When m is 2 or more, two of the groups R^1 to R^6 may be bonded to each other. R^1 s, R^2 s, R^3 s, R^4 s, R^5 s, or R^6 s may be the same as or different from each other.

[0042]

n is a number satisfying a valence of M , specifically an integer of 1 to 3.

X is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group or a silicon-containing group, and

when n is 2 or more, plural groups X may be the same or different.

[0043]

Examples of the halogen atoms include fluorine, chlorine, bromine and iodine.

5 Examples of the hydrocarbon groups of 1 to 20 carbon atoms include alkyl groups, cycloalkyl groups, alkenyl groups, arylalkyl groups and aryl groups. Specifically, there can be mentioned alkyl groups, such as methyl, ethyl, propyl, butyl, hexyl, octyl, nonyl, dodecyl and eicosyl; cycloalkyl groups,
10 such as cyclopentyl, cyclohexyl, norbornyl and adamantyl; alkenyl groups, such as vinyl, propenyl and cyclohexenyl; arylalkyl groups, such as benzyl, phenylethyl and phenylpropyl; and aryl groups, such as phenyl, tolyl, dimethylphenyl, trimethylphenyl, ethylphenyl, propylphenyl,
15 biphenyl, naphthyl, methylnaphthyl, anthryl and phenanthryl.

[0044]

Examples of the halogenated hydrocarbon groups of 1 to 20 carbon atoms include the above-mentioned hydrocarbon groups of 1 to 20 carbon atoms which are substituted with halogens.

20 Examples of the oxygen-containing groups include hydroxyl; alkoxy groups, such as methoxy, ethoxy, propoxy and butoxy; aryloxy groups, such as phenoxy, methylphenoxy, dimethylphenoxy and naphthoxy; and arylalkoxy groups, such as phenylmethoxy and phenylethoxy.

[0045]

Examples of the sulfur-containing groups include groups wherein an oxygen atom of the oxygen-containing groups is substituted with a sulfur atom; sulfonato groups, such as
5 methylsulfonato, trifluoromethanesulfonato, phenylsulfonato, benzylsulfonato, p-toluenesulfonato, trimethylbenzenesulfonato, triisobutylbenzenesulfonato, p-chlorobenzenesulfonato and pentafluorobenzenesulfonato; sulfinato groups, such as
10 methylsulfinato, phenylsulfinato, benzylsulfinato, p-toluenesulfinato, trimethylbenzenesulfinato and pentafluorobenzenesulfinato.

[0046]

Examples of the silicon-containing groups include monohydrocarbon-substituted silyl groups, such as methylsilyl and phenylsilyl; dihydrocarbon-substituted silyl groups, such
15 as dimethylsilyl and diphenylsilyl; trihydrocarbon-substituted silyl groups, such as trimethylsilyl, triethylsilyl, tripropylsilyl, tricyclohexylsilyl, triphenylsilyl, dimethylphenylsilyl, methyldiphenylsilyl, tritolylsilyl and trinaphthylsilyl; hydrocarbon-substituted silylether groups,
20 such as trimethylsilylether; silicon-substituted alkyl groups, such as trimethylsilylmethyl; and silicon-substituted aryl groups, such as trimethylsilylphenyl.

[0047]

Of these, preferable are hydrocarbon groups of 1 to 20

halogen atoms or carbon atoms, or sulfonato groups.

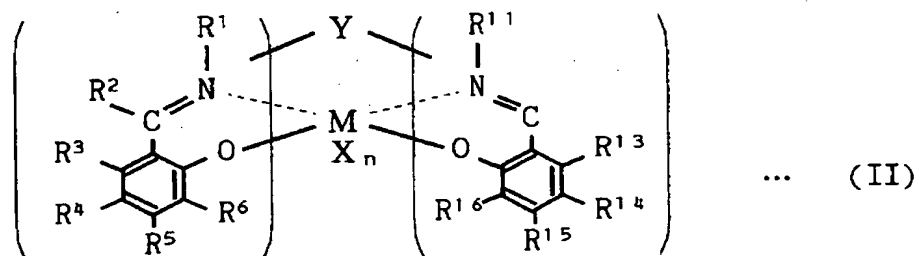
When n is 2 or more, groups X may be bonded to each other to form a ring.

[0048]

5 In the transition metal compounds represented by the formula (I), the compound wherein m is 2 and two of the groups R^1 to R^6 are bonded to each other is, for example, a compound represented by the following formula (II).

[0049]

10



15 [0050]

In the above formula, M, R^1 to R^6 , and X are identical with M, R^1 to R^6 , and X in the formula (I).

R^{11} to R^{16} may be the same or different, and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a heterocyclic compound residue, a hydrocarbon-substituted silyl group, a hydrocarbon-substituted siloxy group, an alkoxy group, an thioalkoxy group, an aryloxy group, an thioaryloxy group, an acyl group, an ester group, a thioester group, an amido group, an imido group, an amino group, an imino group,

20

a sulfonester group, a sulfonamido group, a cyano group or a nitro group, specifically, the same atom or group as described for R^1 to R^6 . Two or more of these, preferably adjacent groups, may be bonded to each other to form an aliphatic ring, an aromatic ring or a hydrocarbon ring containing a hetero atom such as a nitrogen atom.

[0051]

Y is a bonding group or a single bond for bonding at least one group selected from R^1 to R^6 to at least one group selected from R^{11} to R^{16} (except a case of bonding R^1 and R^{11} to each other).

[0052].

The bonding group Y is a group containing at least one element selected from among oxygen, sulfur, carbon, nitrogen, phosphorus, silicon, selenium, tin, boron and the like. Examples of such groups include chalcogen atom-containing groups such as -O-, -S- and -Se-; nitrogen- or phosphorus-containing groups, such as -NH-, -N(CH₃)₂-, -PH- and -P(CH₃)₂-; hydrocarbon groups of 1 to 20 carbon atoms, such as -CH₂-, -CH₂-CH₂- and -C(CH₃)₂-; residues of cyclic hydrocarbons of 6 to 20 carbon atoms, such as benzene, naphthalene and anthracene; residues of heterocyclic compounds having 3 to 20 carbon atoms and containing hetero atoms, such as pyridine, quinoline, thiophene and furan; silicon atom-containing groups, such as -SiH₂- and -Si(CH₃)₂-; tin atom-containing

groups, such as $-\text{SnH}_2-$ and $-\text{Sn}(\text{CH}_3)_2-$; and boron atom-containing groups, such as $-\text{BH}-$, $-\text{B}(\text{CH}_3)-$ and $-\text{BF}-$.

[0053]

Examples of the transition metal compounds represented
5 by the formula (I) are given below, but are not limited thereto.

In the following examples, M is a transition metallic element, and specifically represents, but not limited to, Sc(III), Ti(III)(IV), Zr(III)(IV), Hf(IV), V(IV), Nb(V), Ta(V), Co(II)(III), Ni(II), Rh(II)(III)(IV) or Pd(II)(VI).
10 Of these, particularly preferable is Ti(IV), Zr(IV) or Hf(IV).

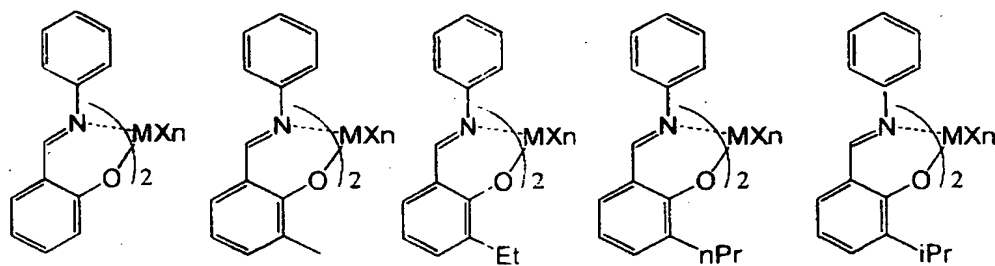
[0054]

X is halogen such as Cl or Br, or an alkyl group such as methyl, but not limited thereto. When plural X are present, they may be the same or different.

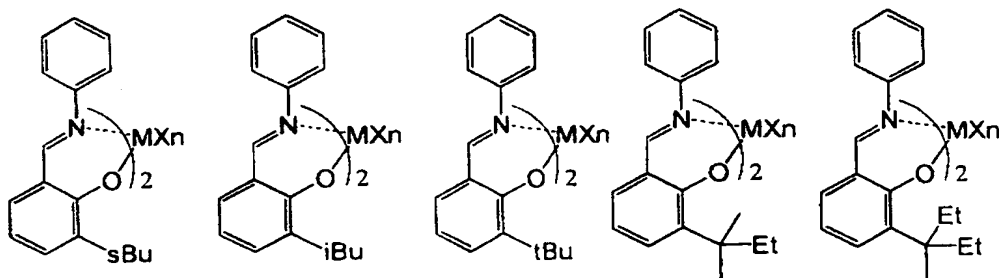
15 [0055]

n depends on a valence of the metal. For example, when two monoanion species are bonded to the metal, $n = 0$ in case of a divalent metal, $n = 1$ in case of a trivalent metal, $n = 2$ in case of a tetravalent metal, and $n = 3$ in case of a
20 pentavalent metal. More specifically, there can be mentioned $n = 2$ in case of Ti(IV), $n = 2$ in case of Zr(IV), and $n = 2$ in case of Hf(IV).

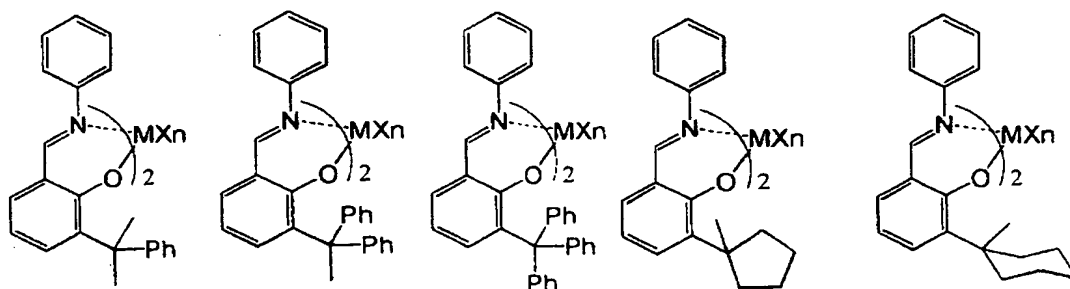
[0056]



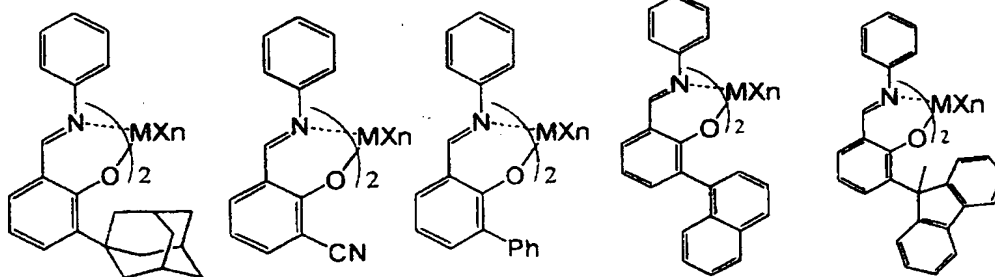
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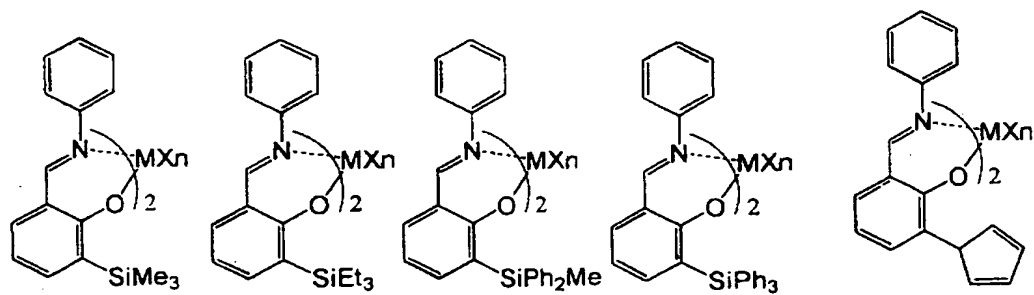
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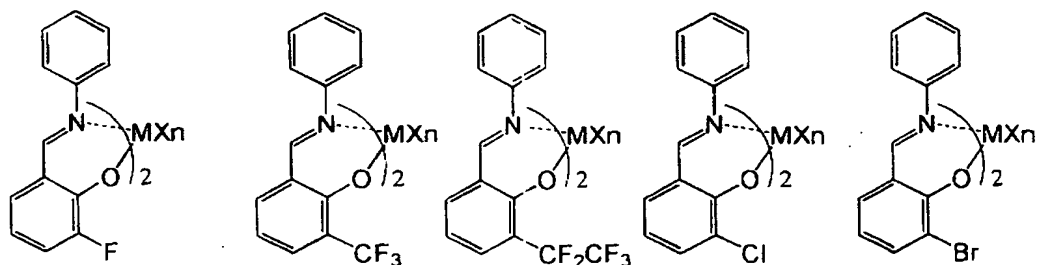


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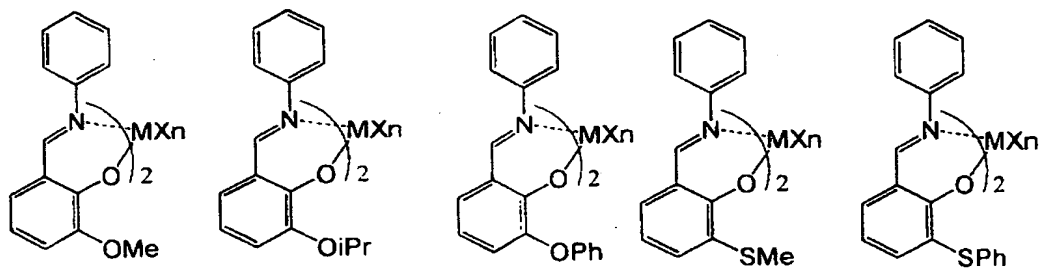


[0057]

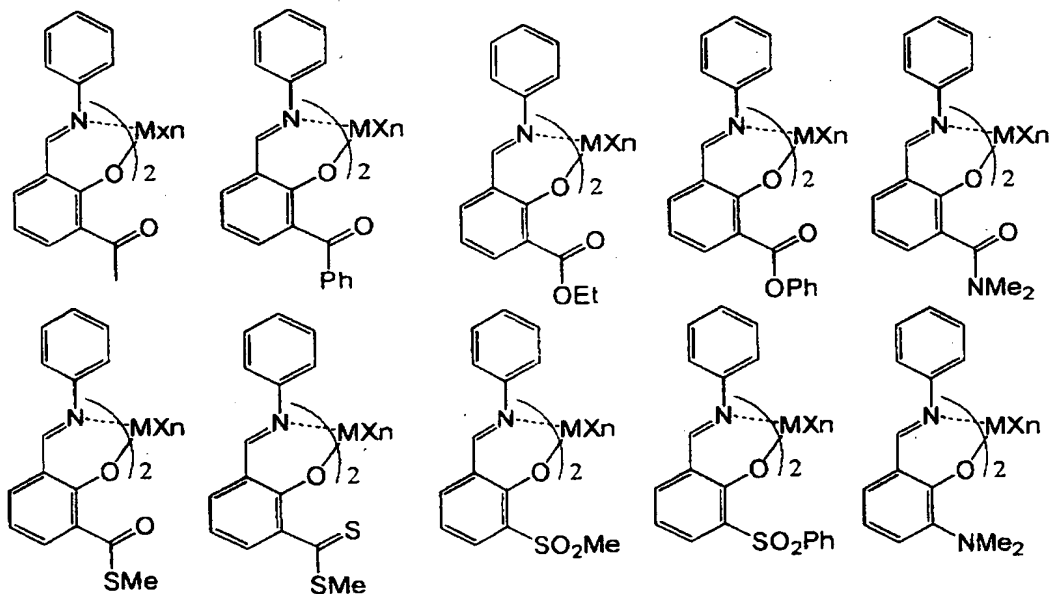
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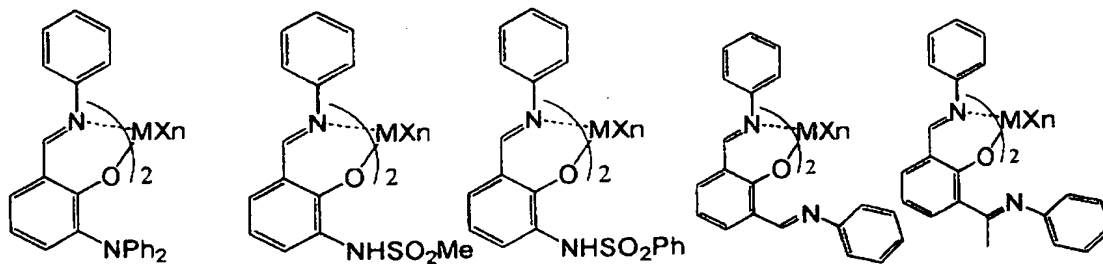
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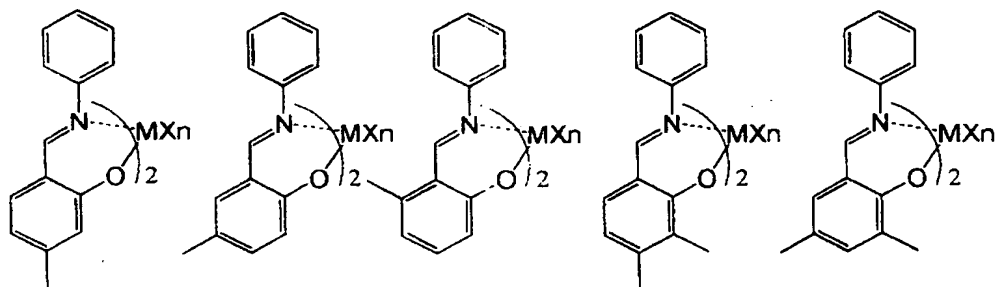


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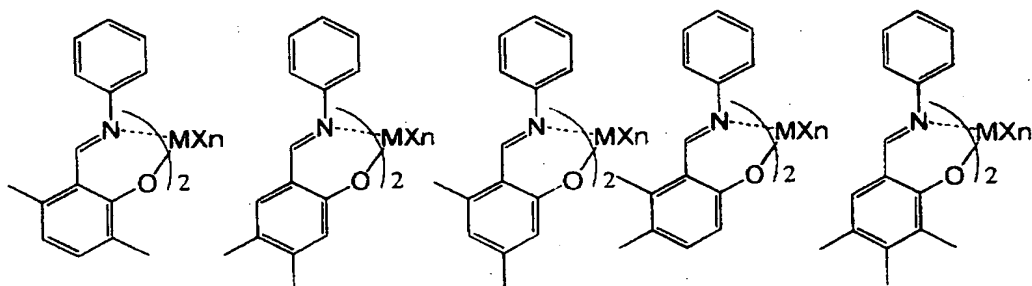


[0058]

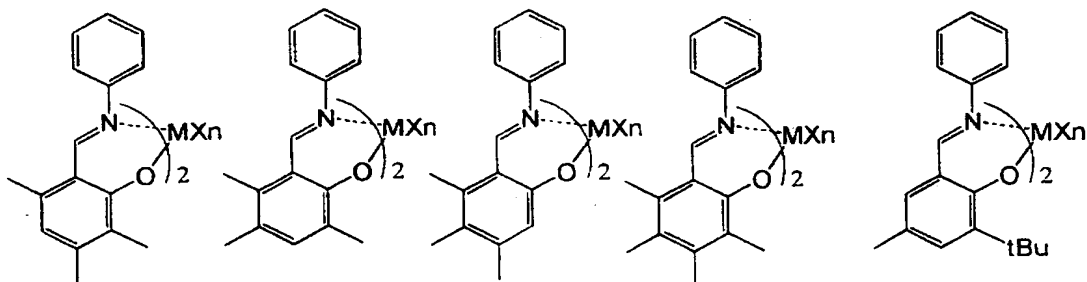
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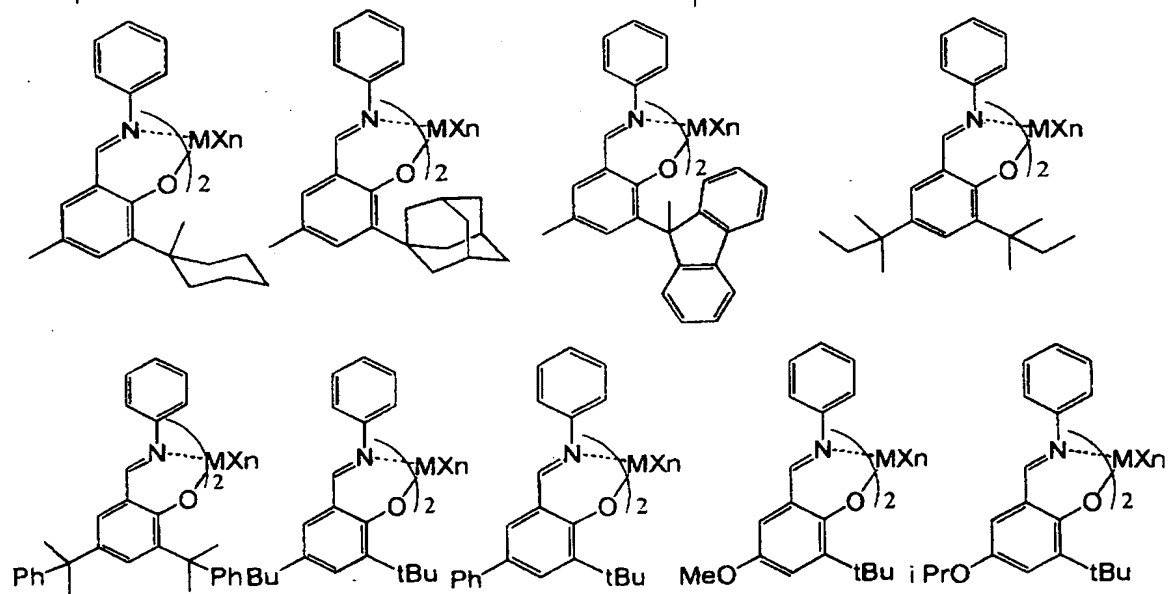
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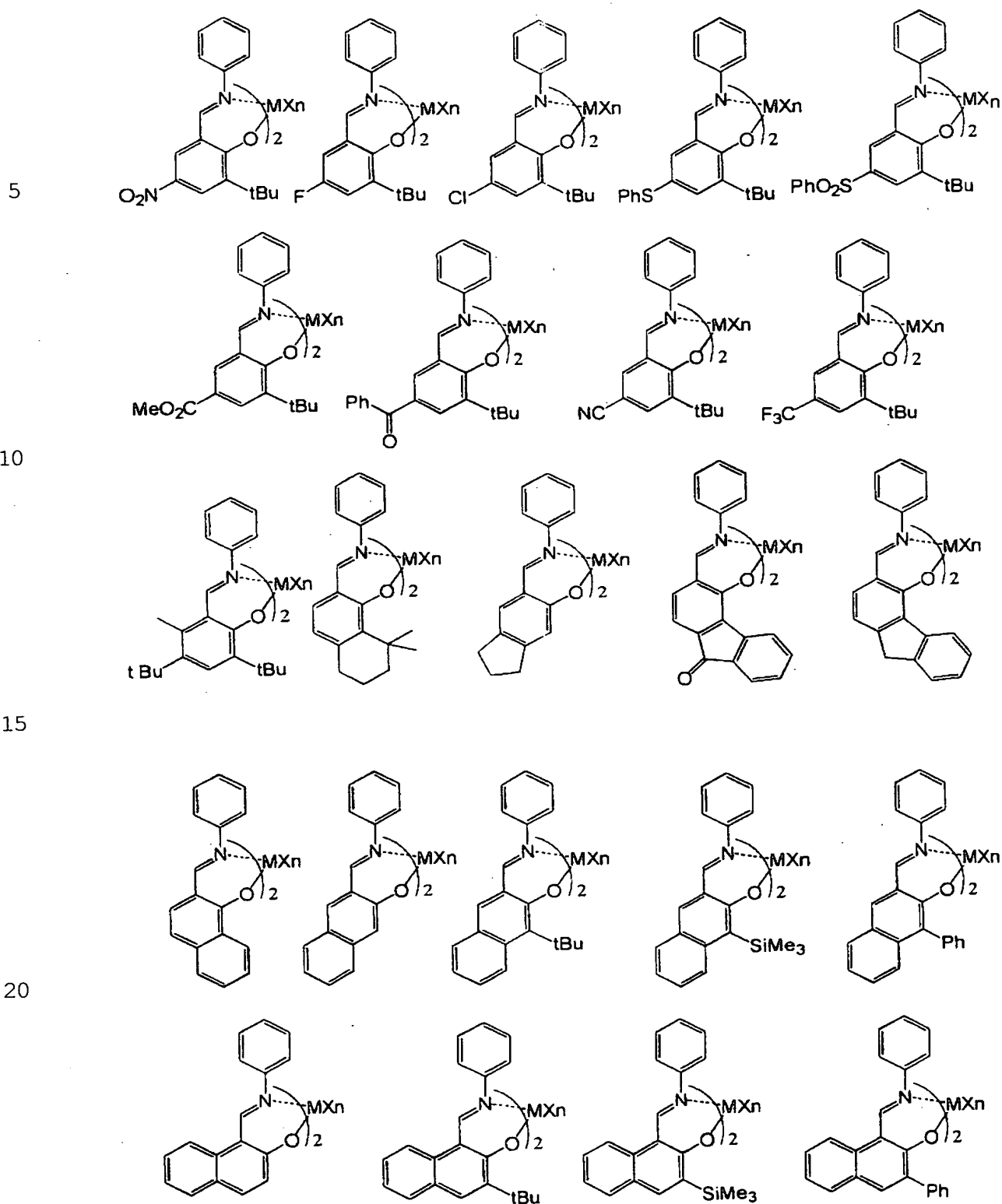
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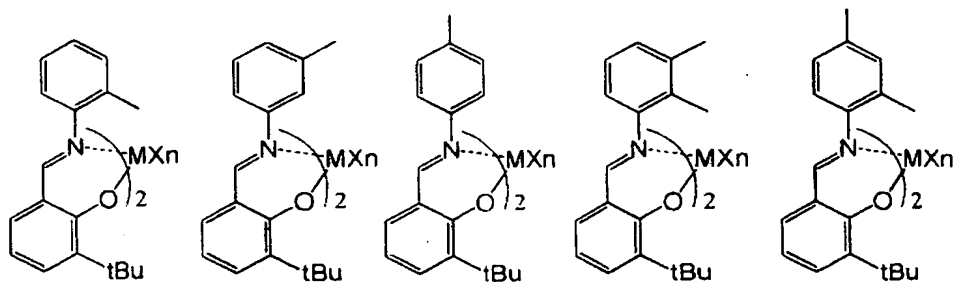


[0059]

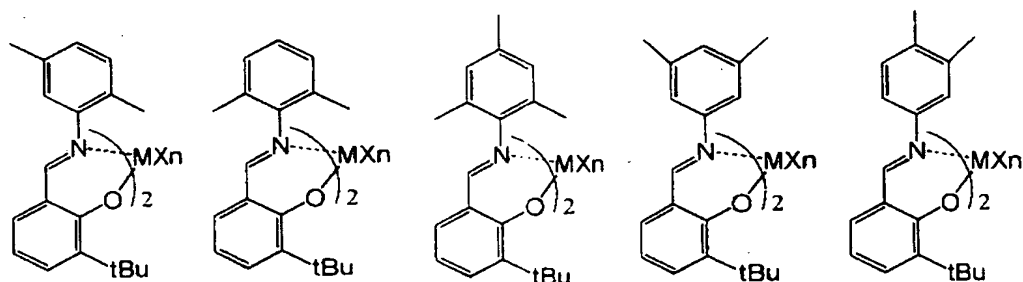


[0060]

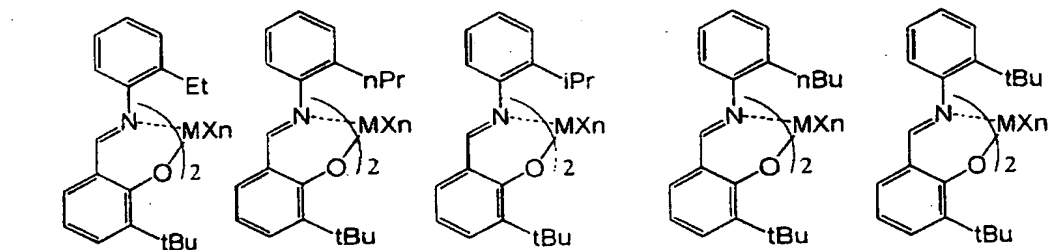
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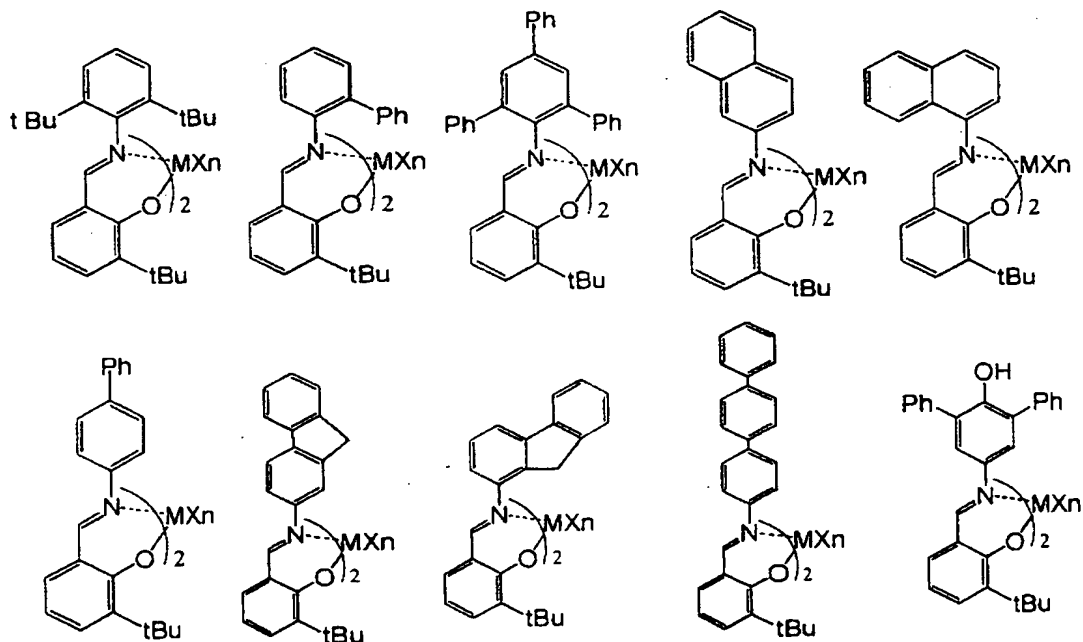
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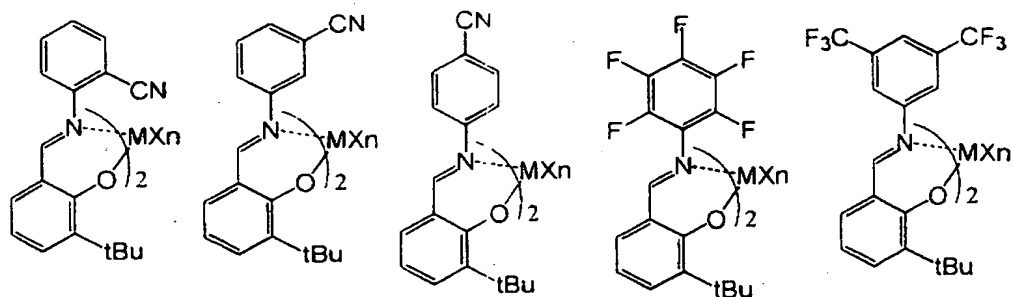


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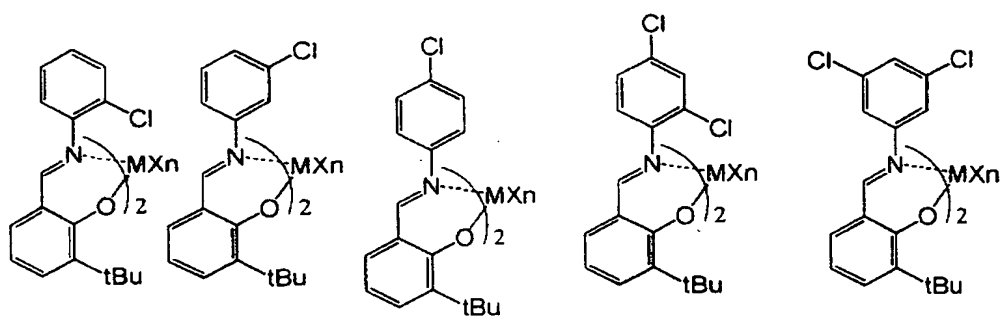


[0061]

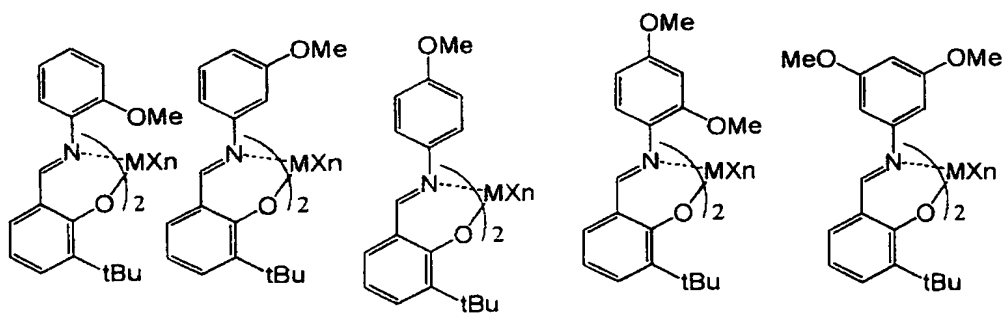
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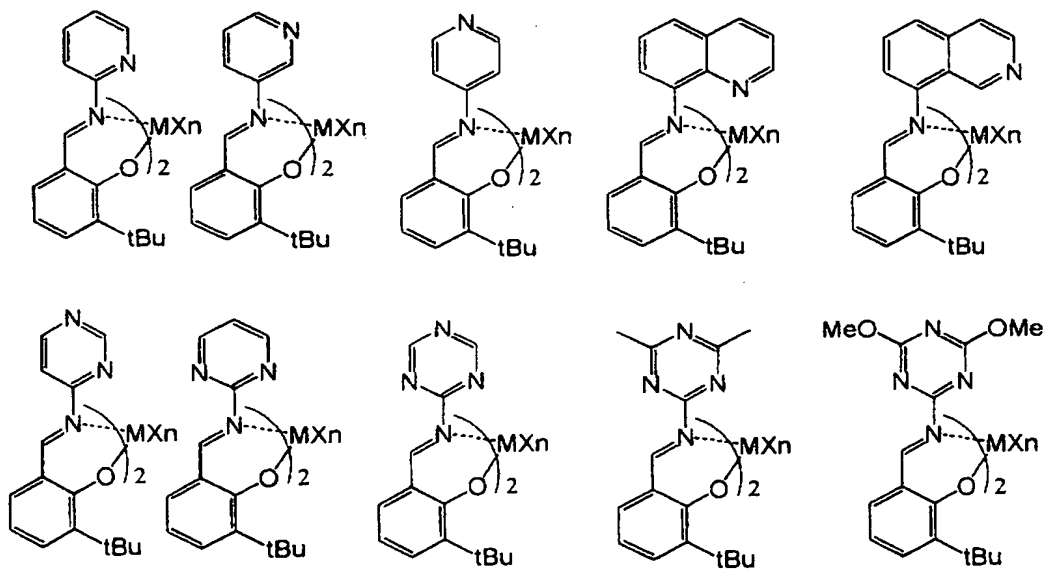
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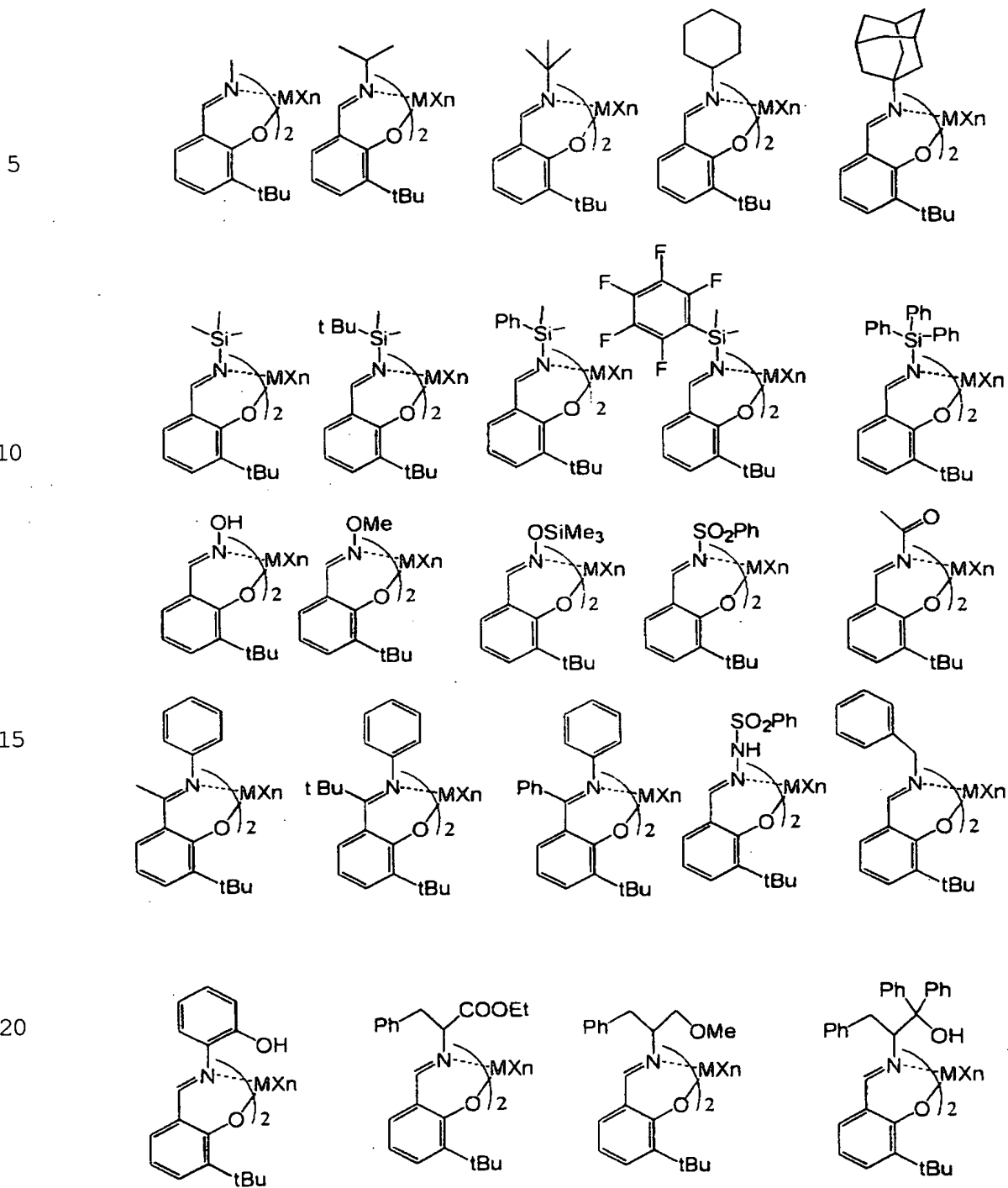
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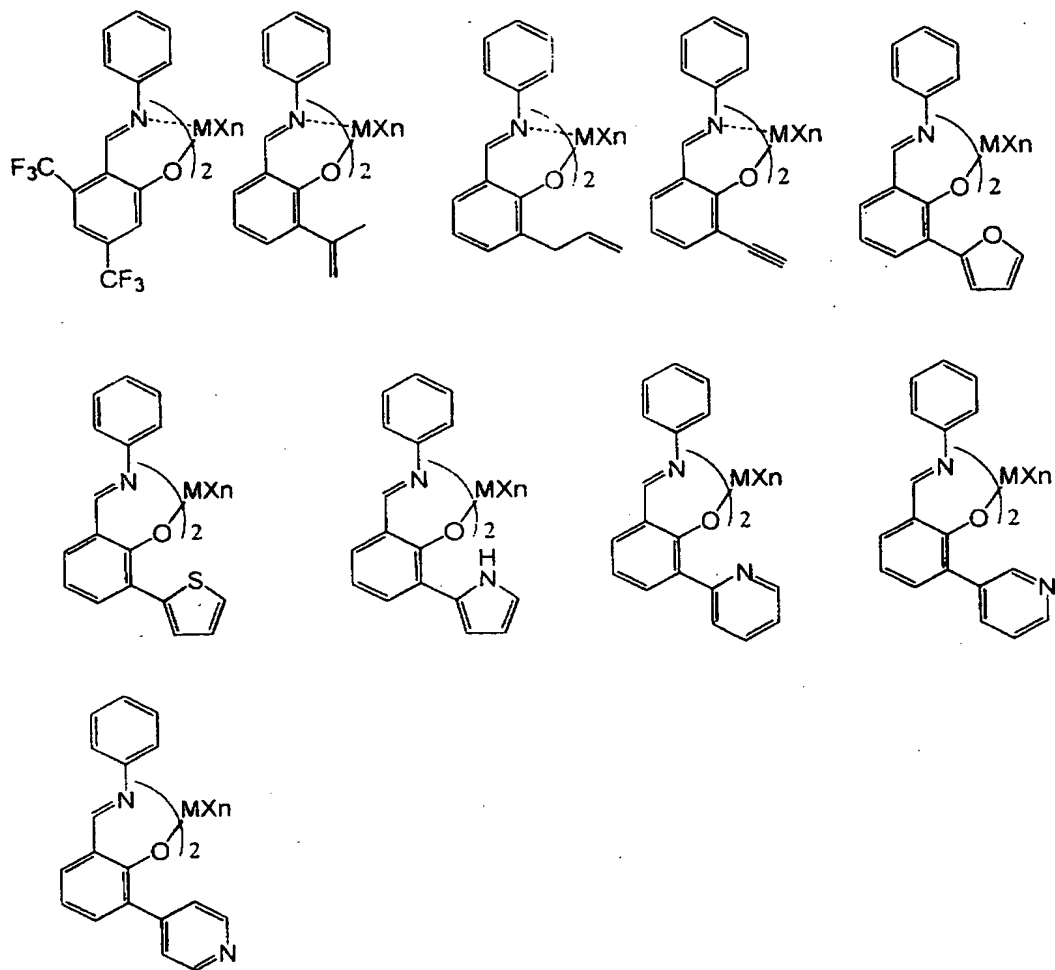
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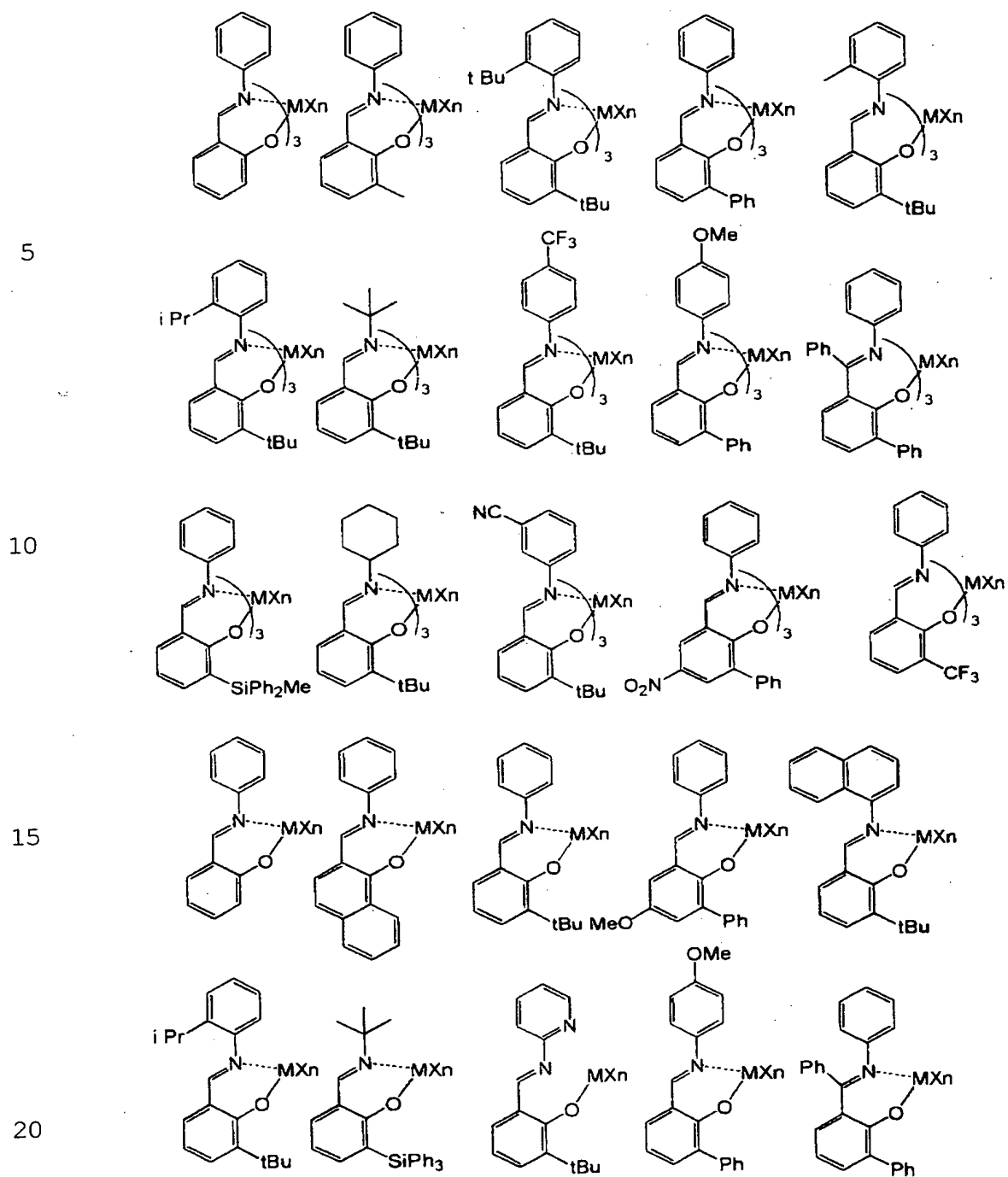
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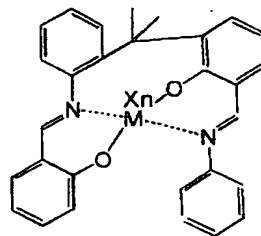
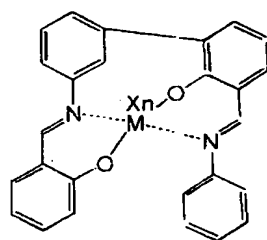
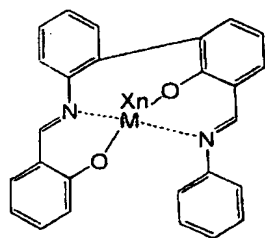


[0063]

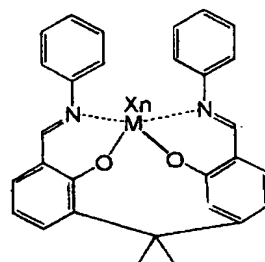
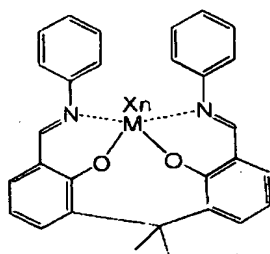
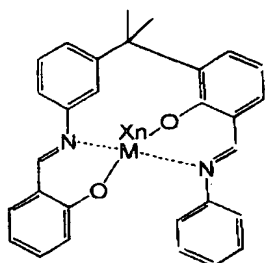


[0064]

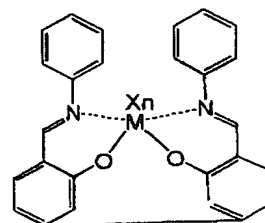
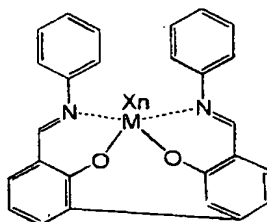
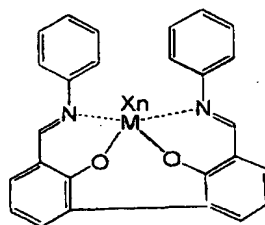




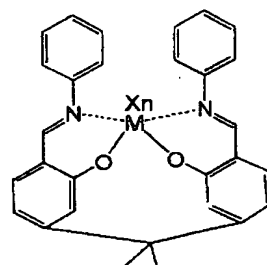
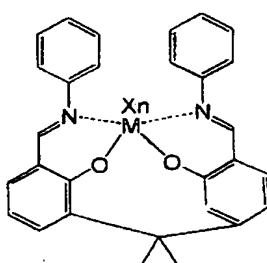
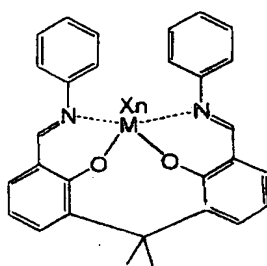
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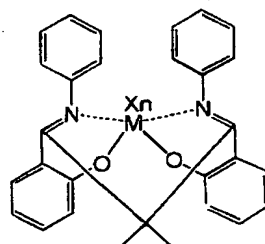
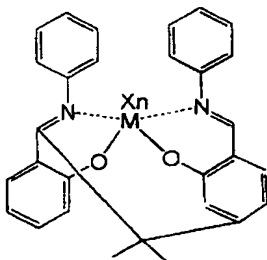
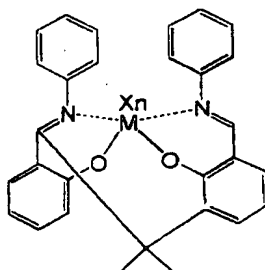
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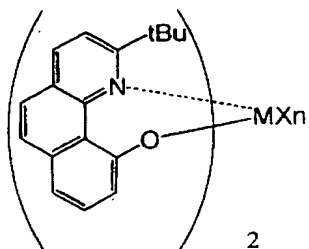
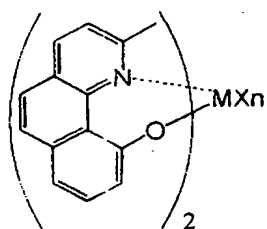
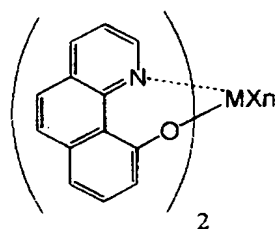


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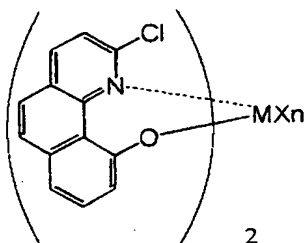
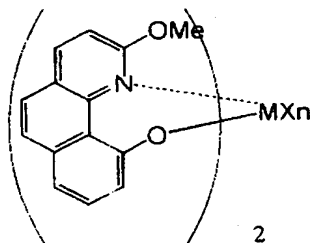
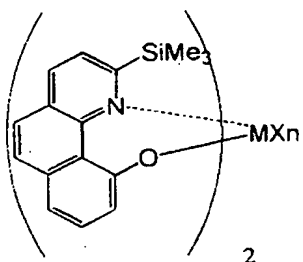


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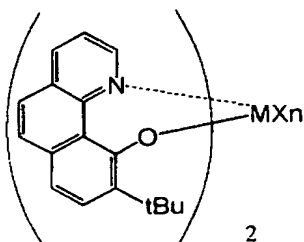
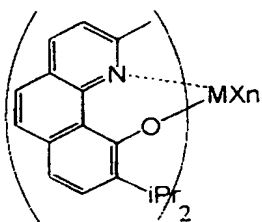
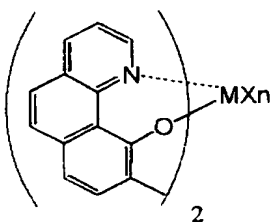




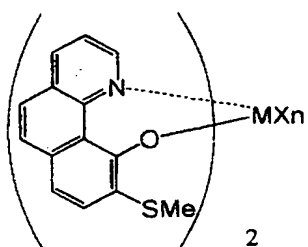
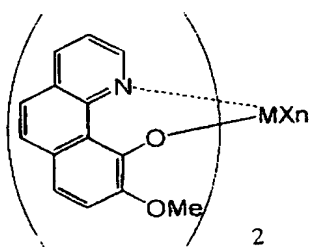
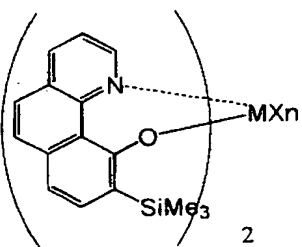
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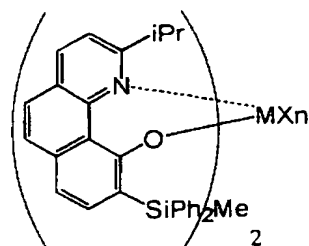
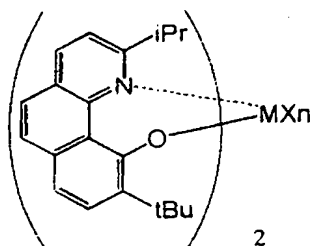
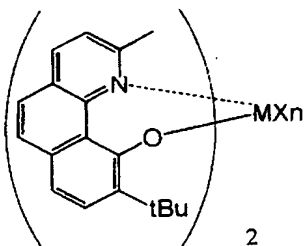
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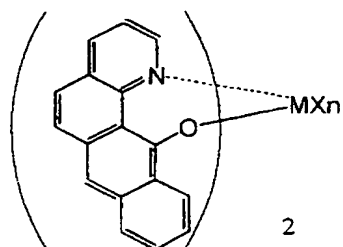
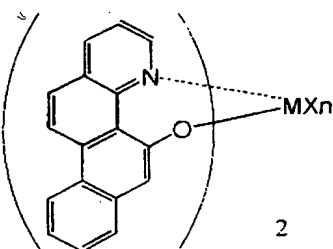
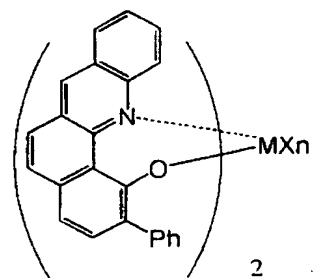
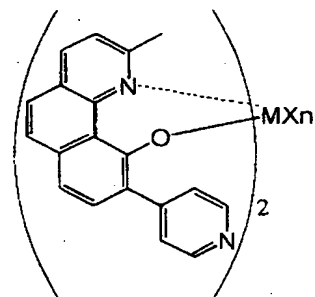
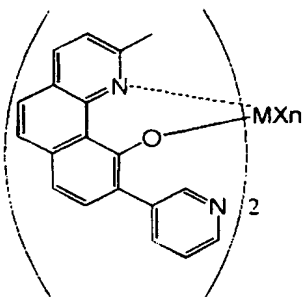
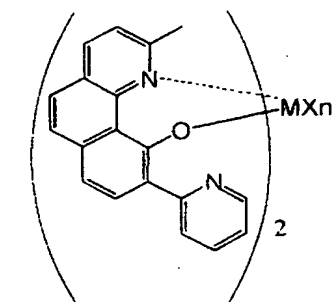
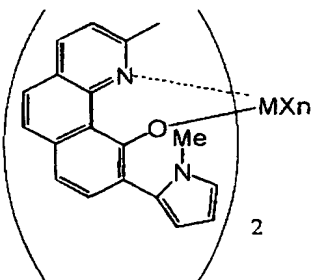
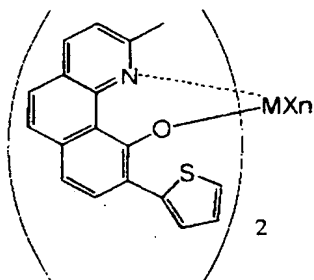
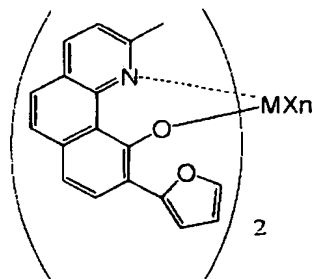
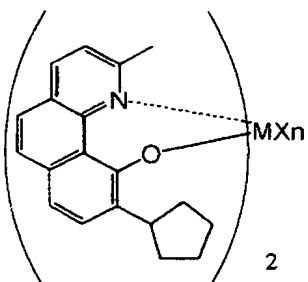
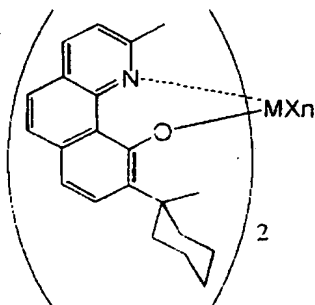
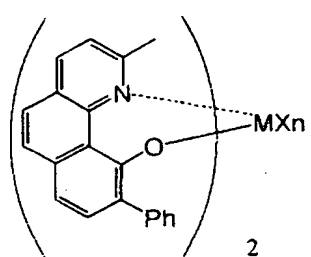


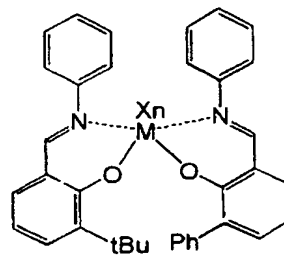
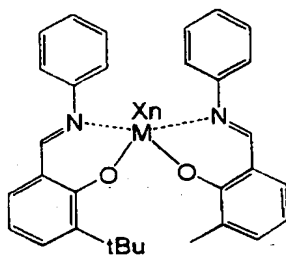
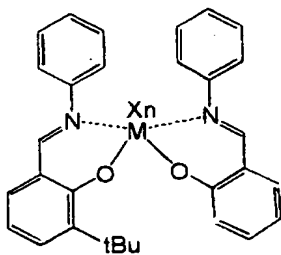
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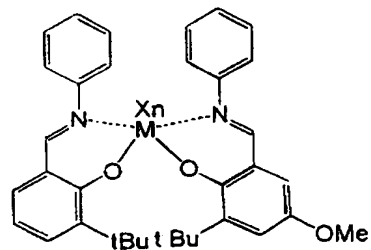
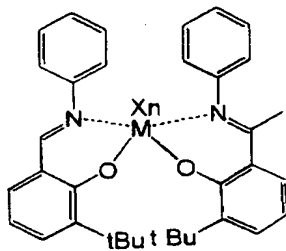
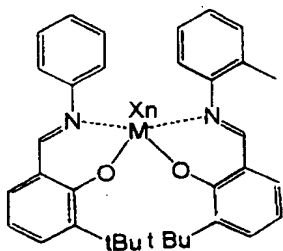
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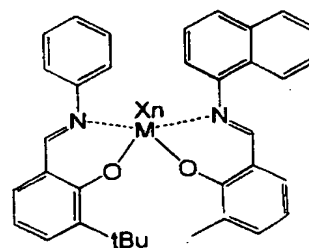
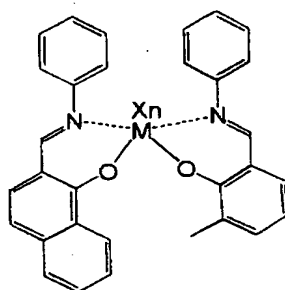
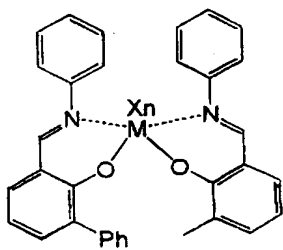




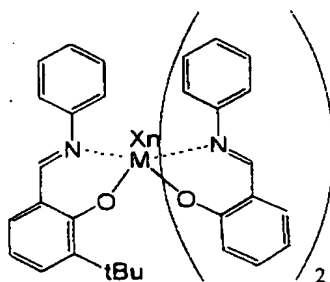
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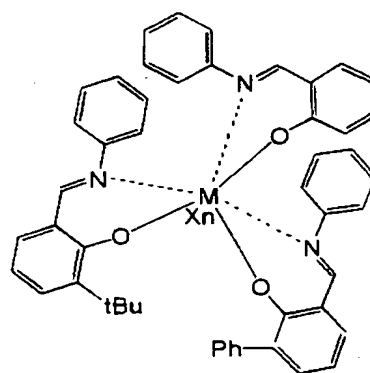
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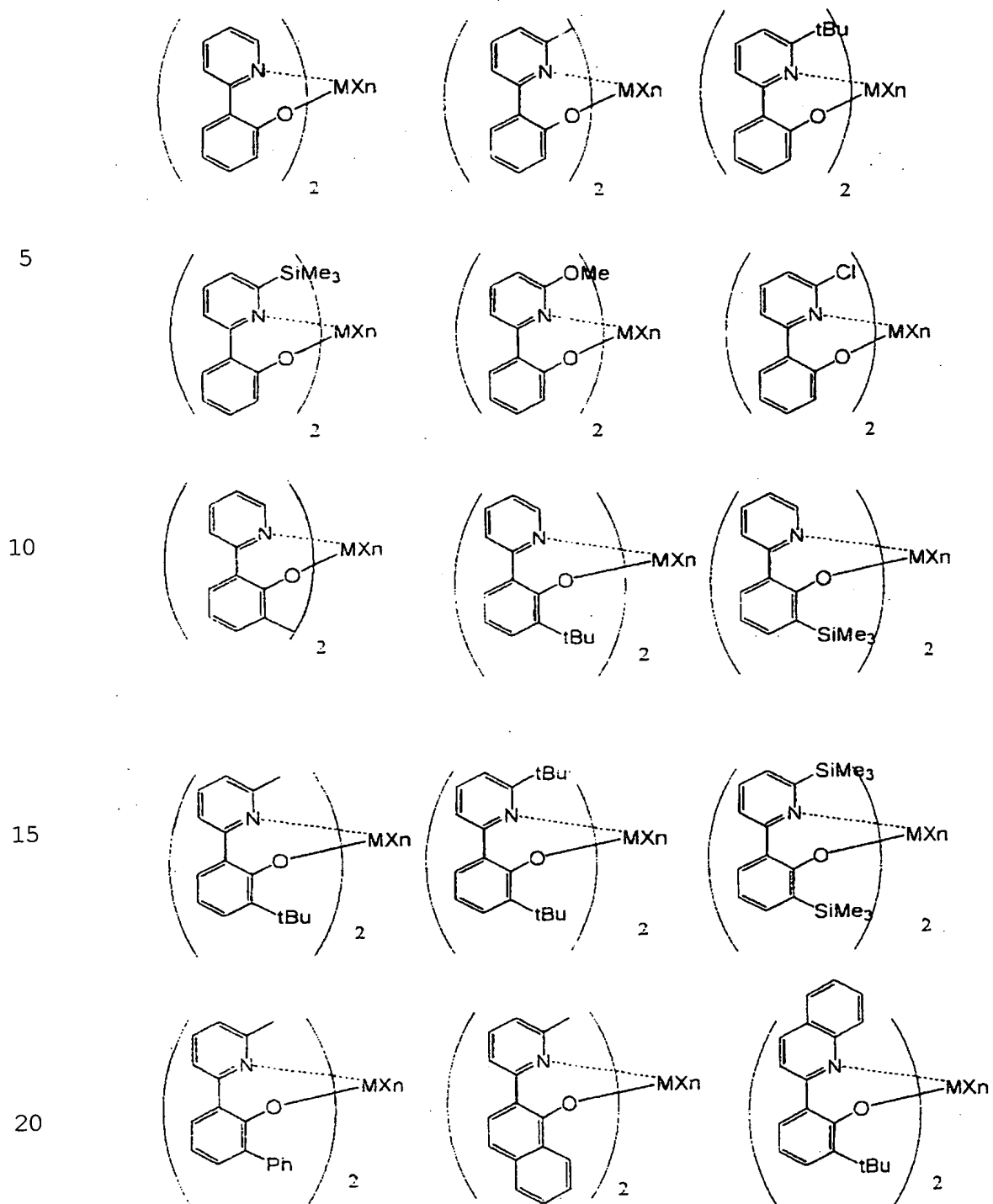


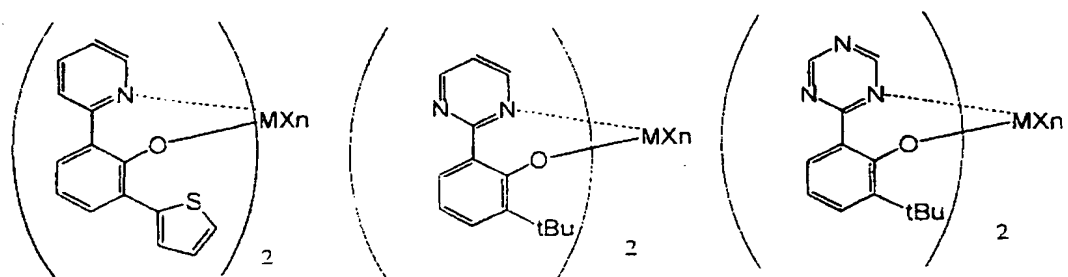
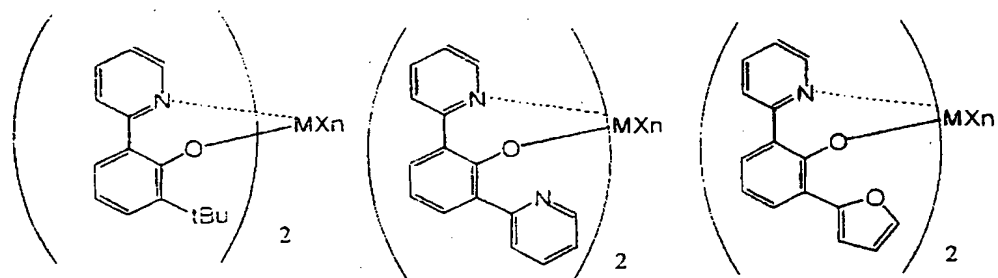
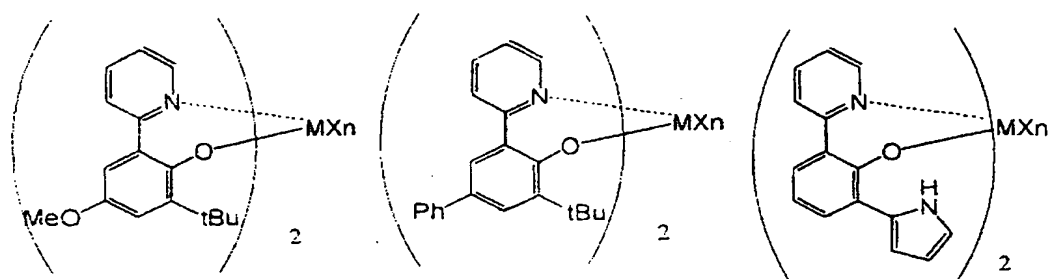
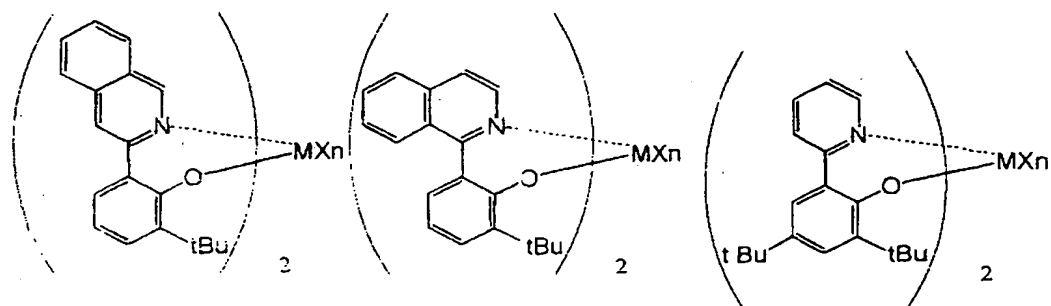
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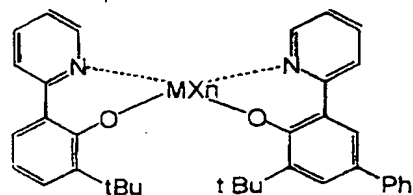
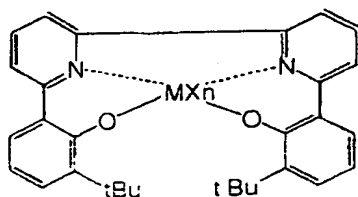


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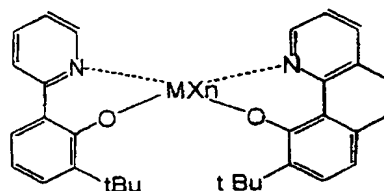
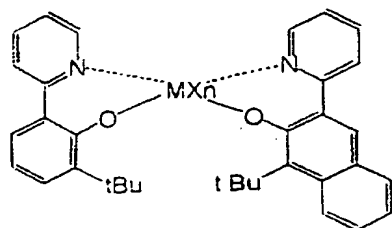




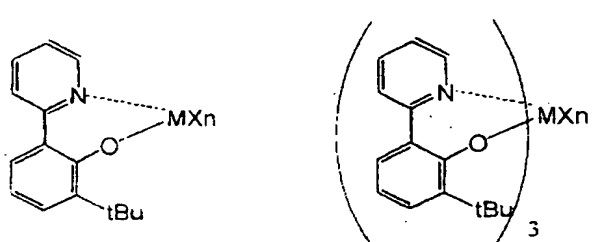
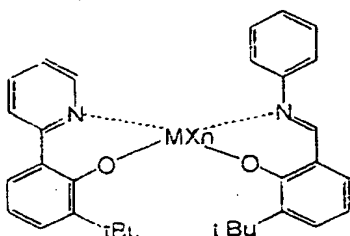




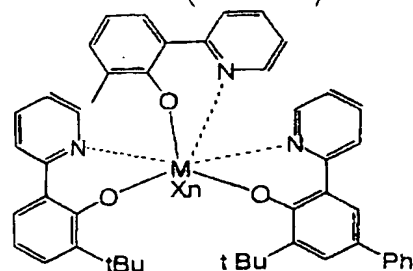
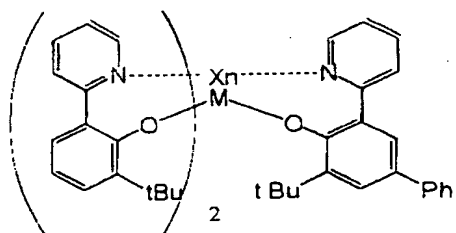
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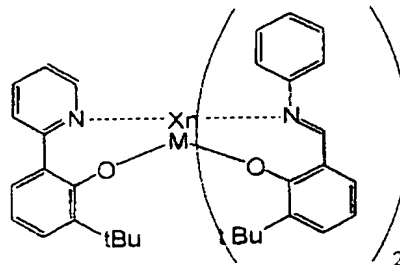
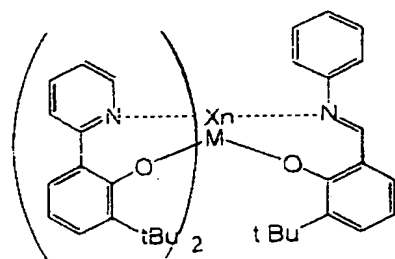
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[0072]

In the above exemplification, Et is ethyl, iPr is isopropyl, tBu is tert-butyl and Ph is phenyl.

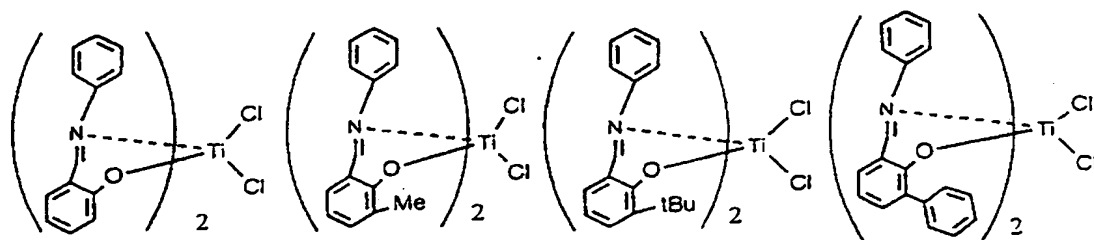
More specific examples of compounds having a center metal Ti are given below. There can also be mentioned those compounds in which titanium is replaced with zirconium, hafnium, cobalt or rhodium.

5 [0073]

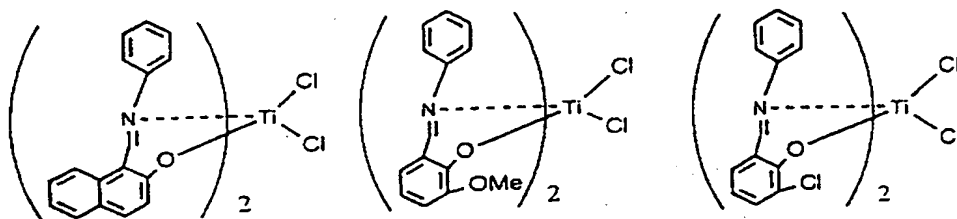
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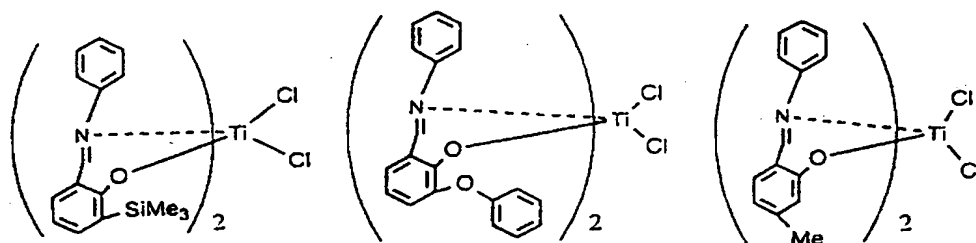
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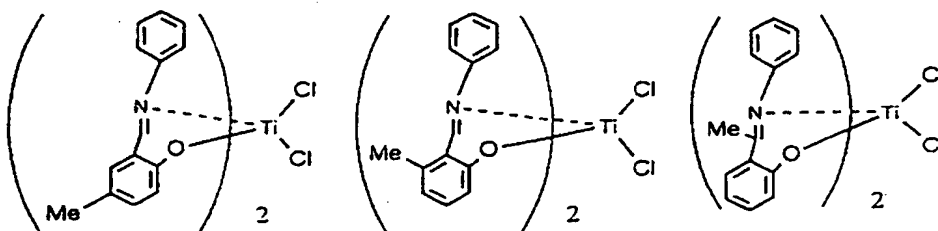
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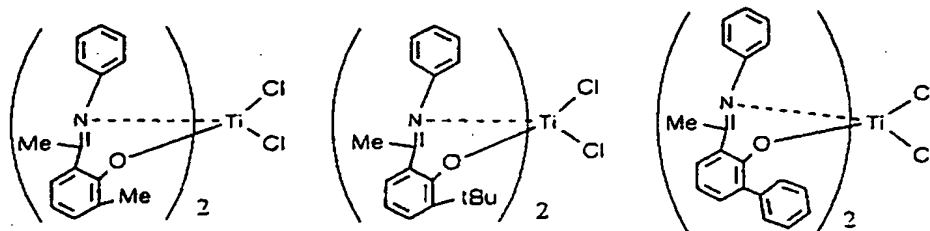
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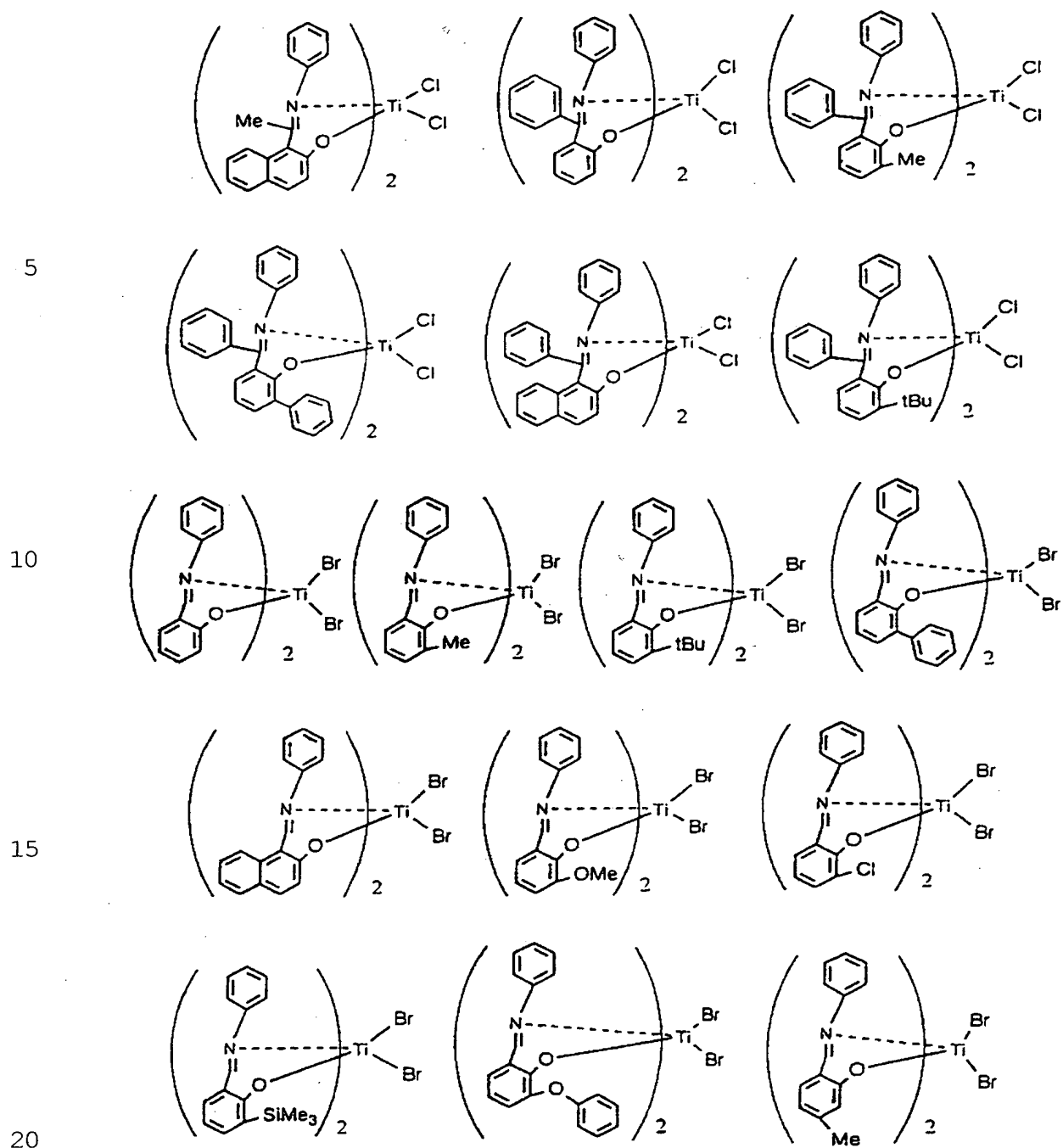


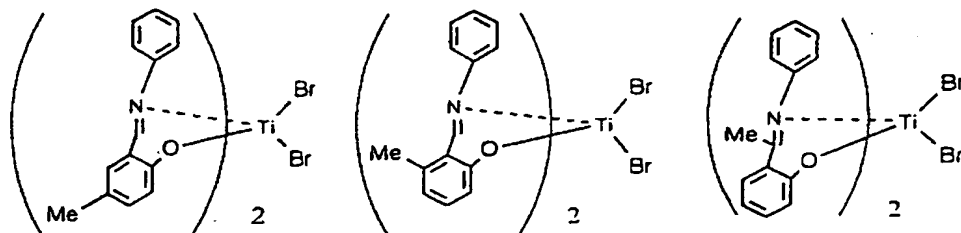
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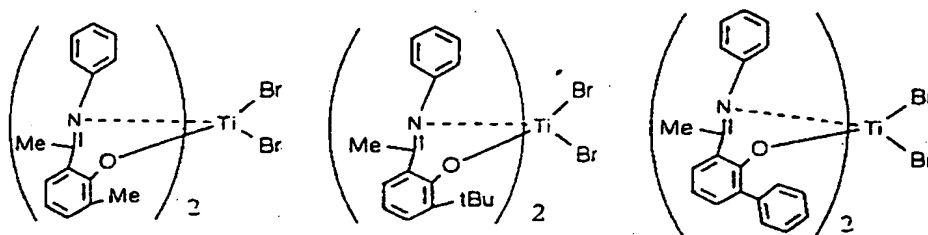
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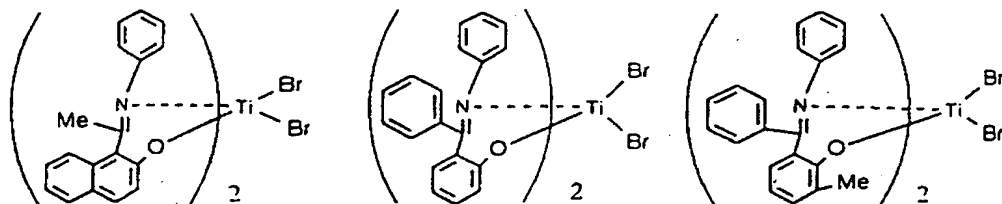




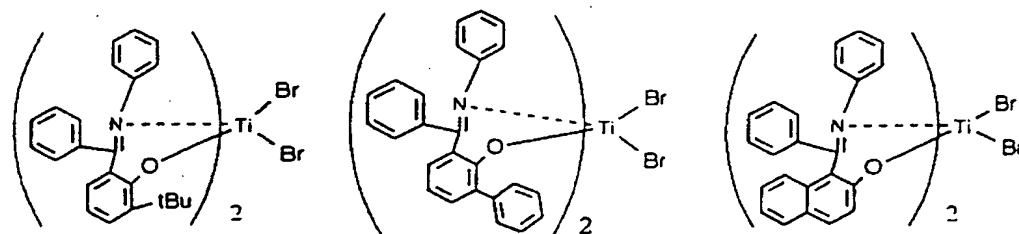
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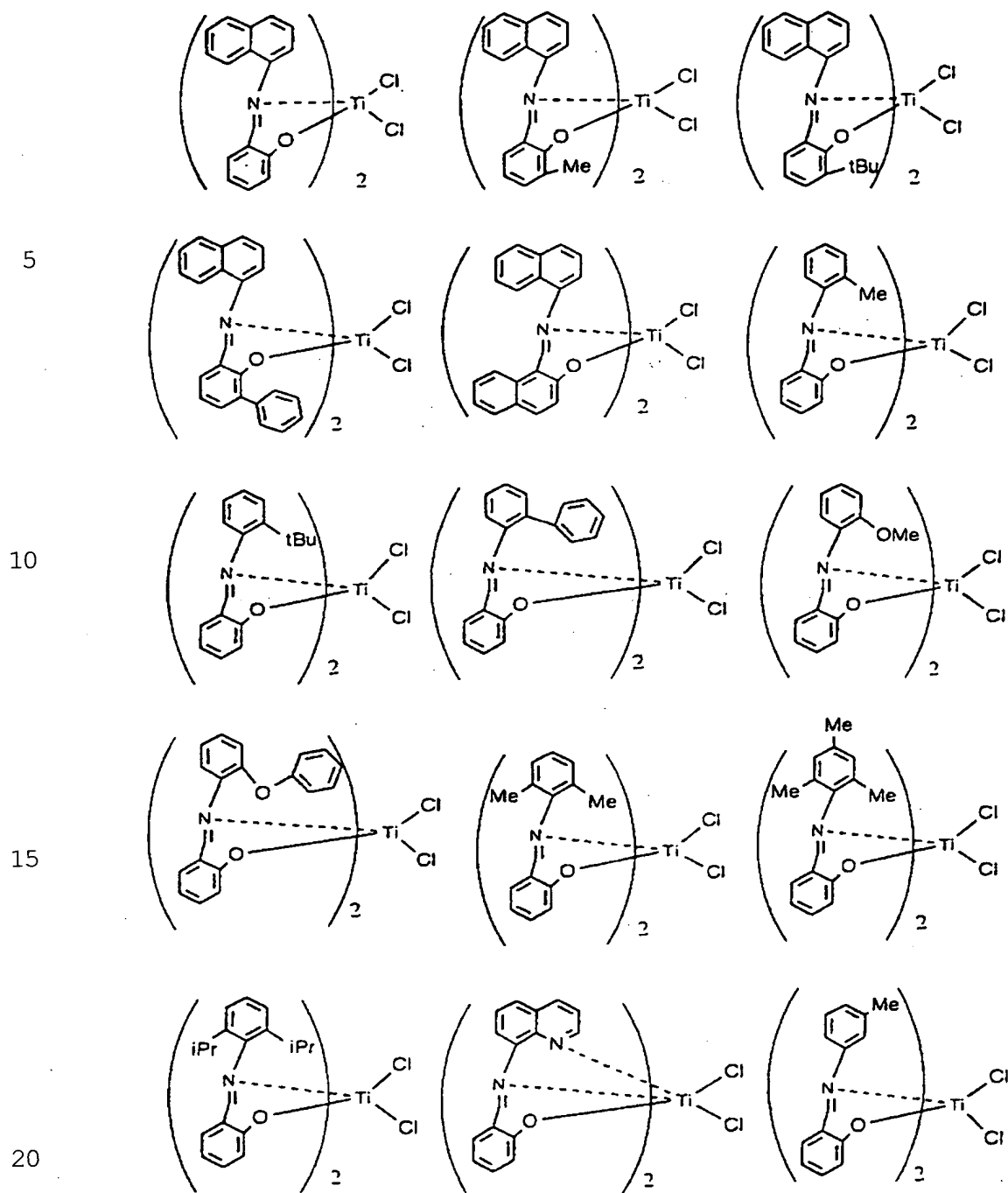


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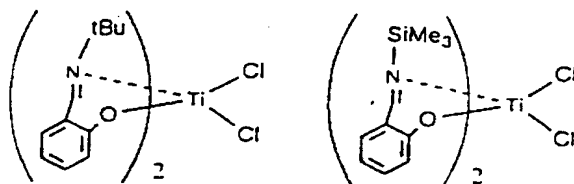
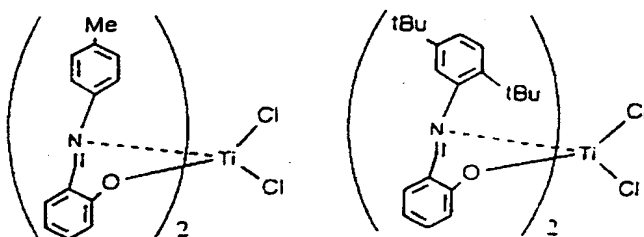


[0076]

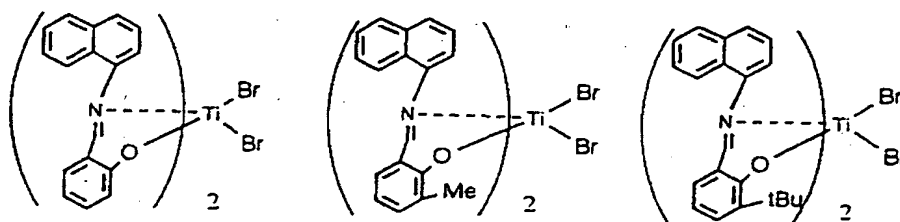
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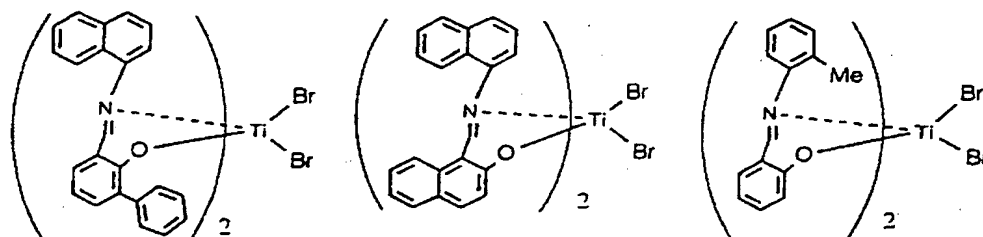
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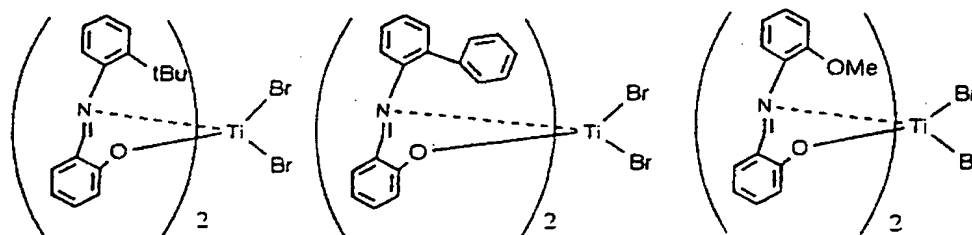
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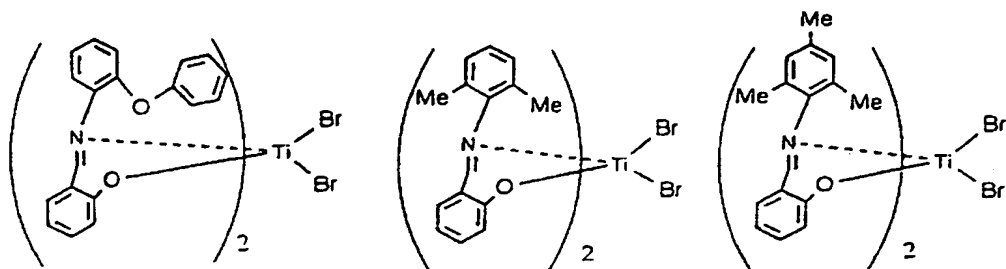


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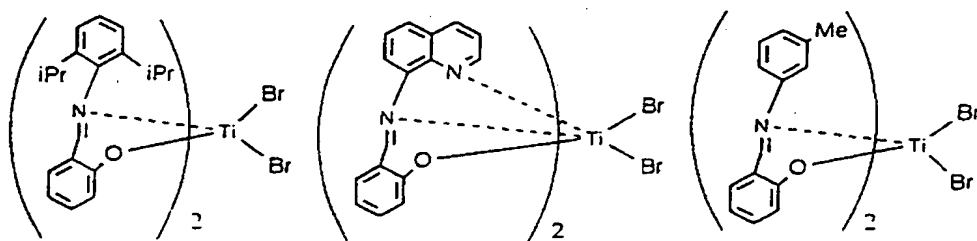


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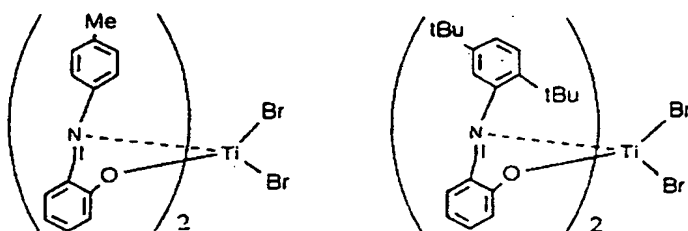




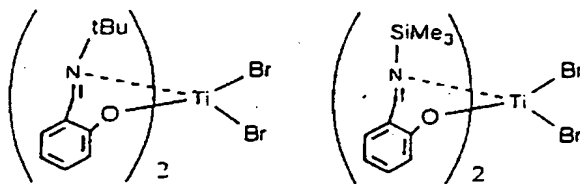
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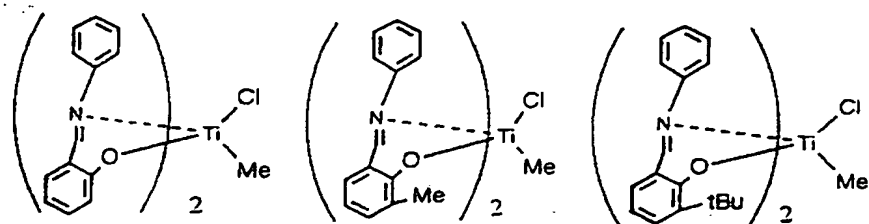


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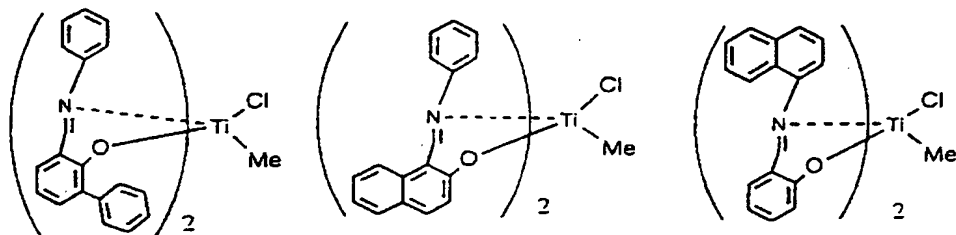


[0079]

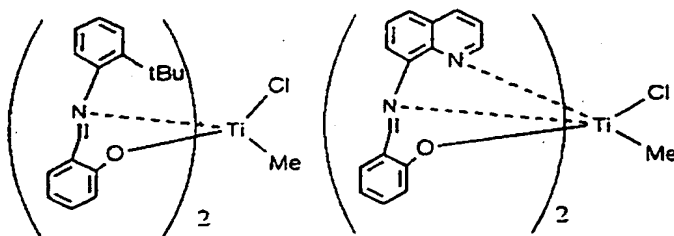
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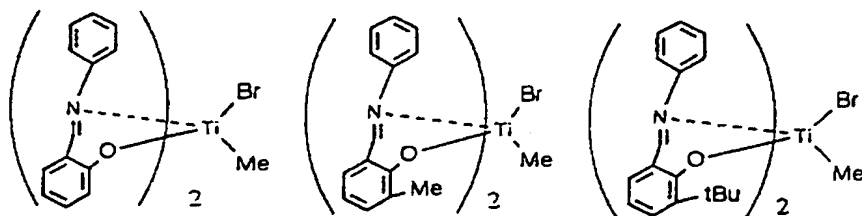
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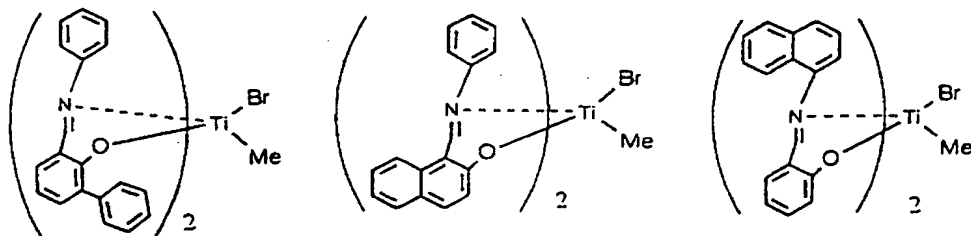
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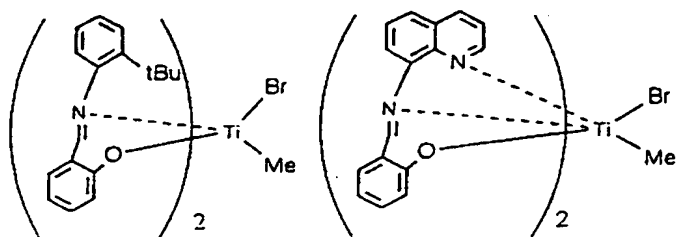
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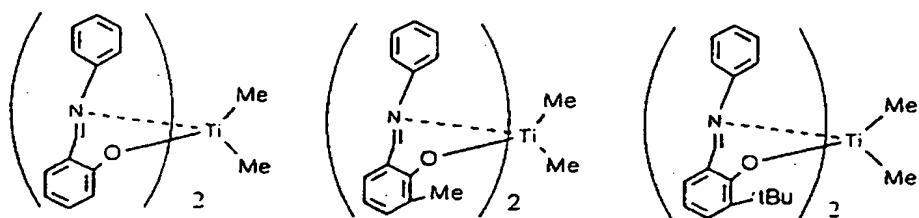
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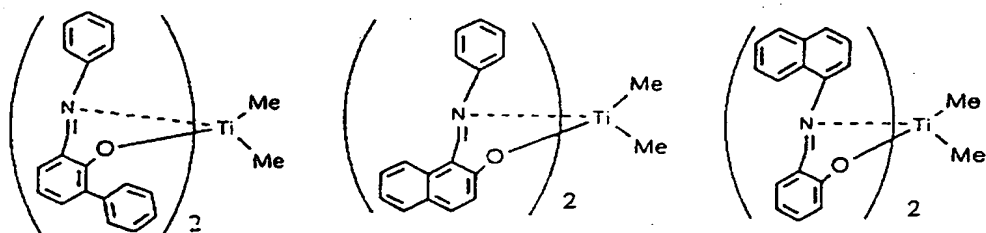
[0080]



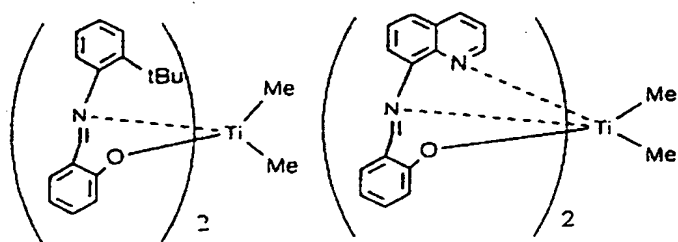
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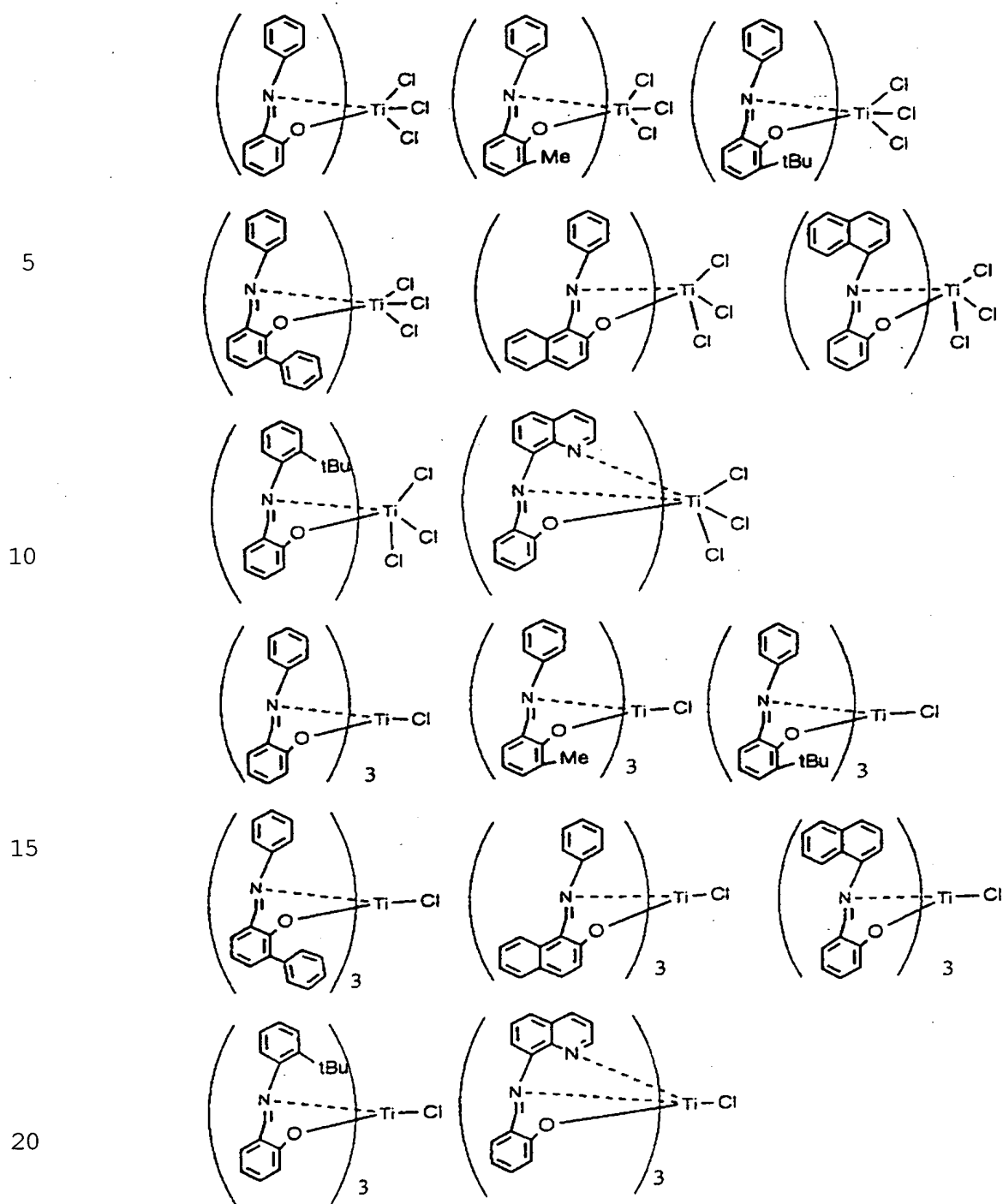


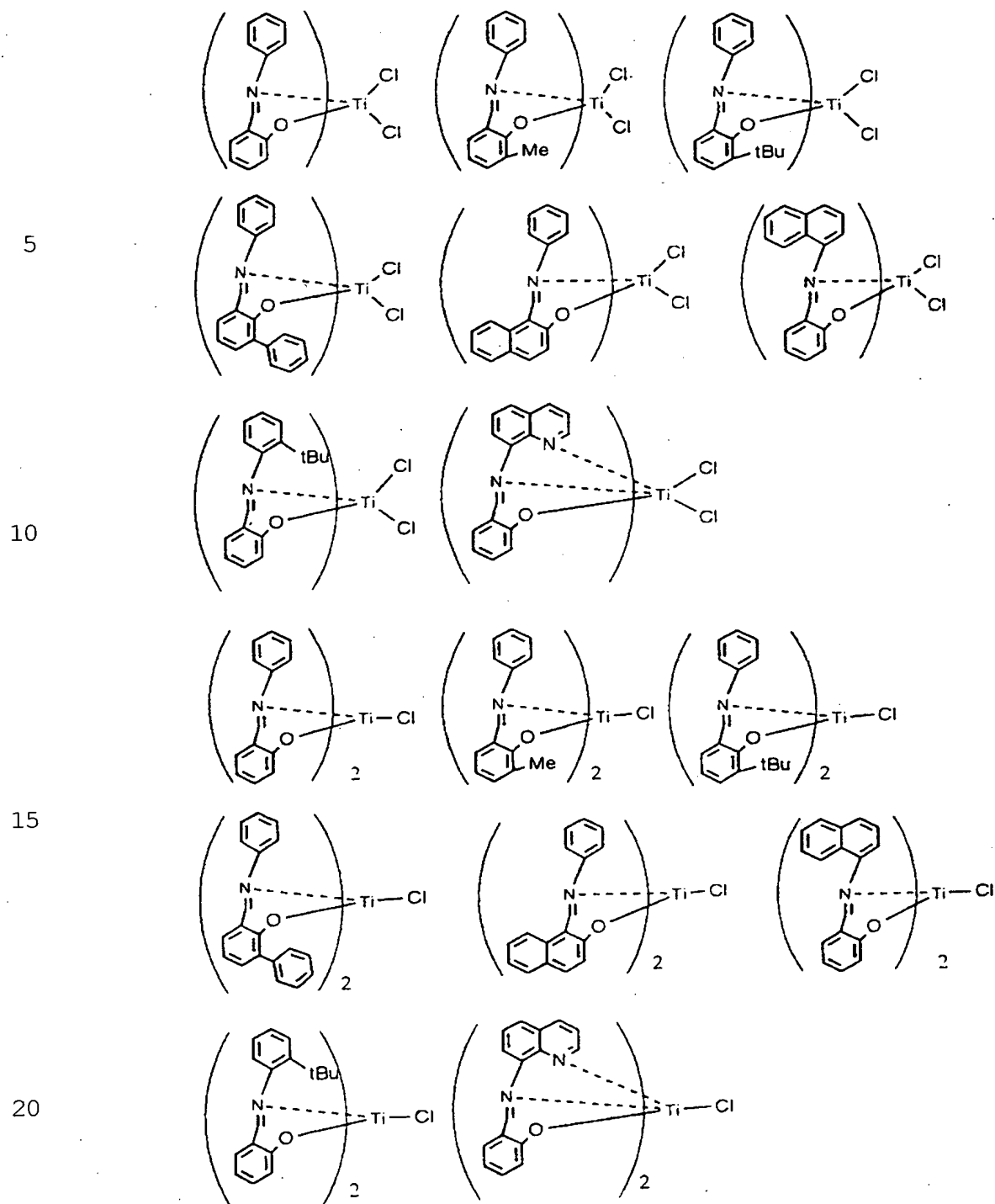
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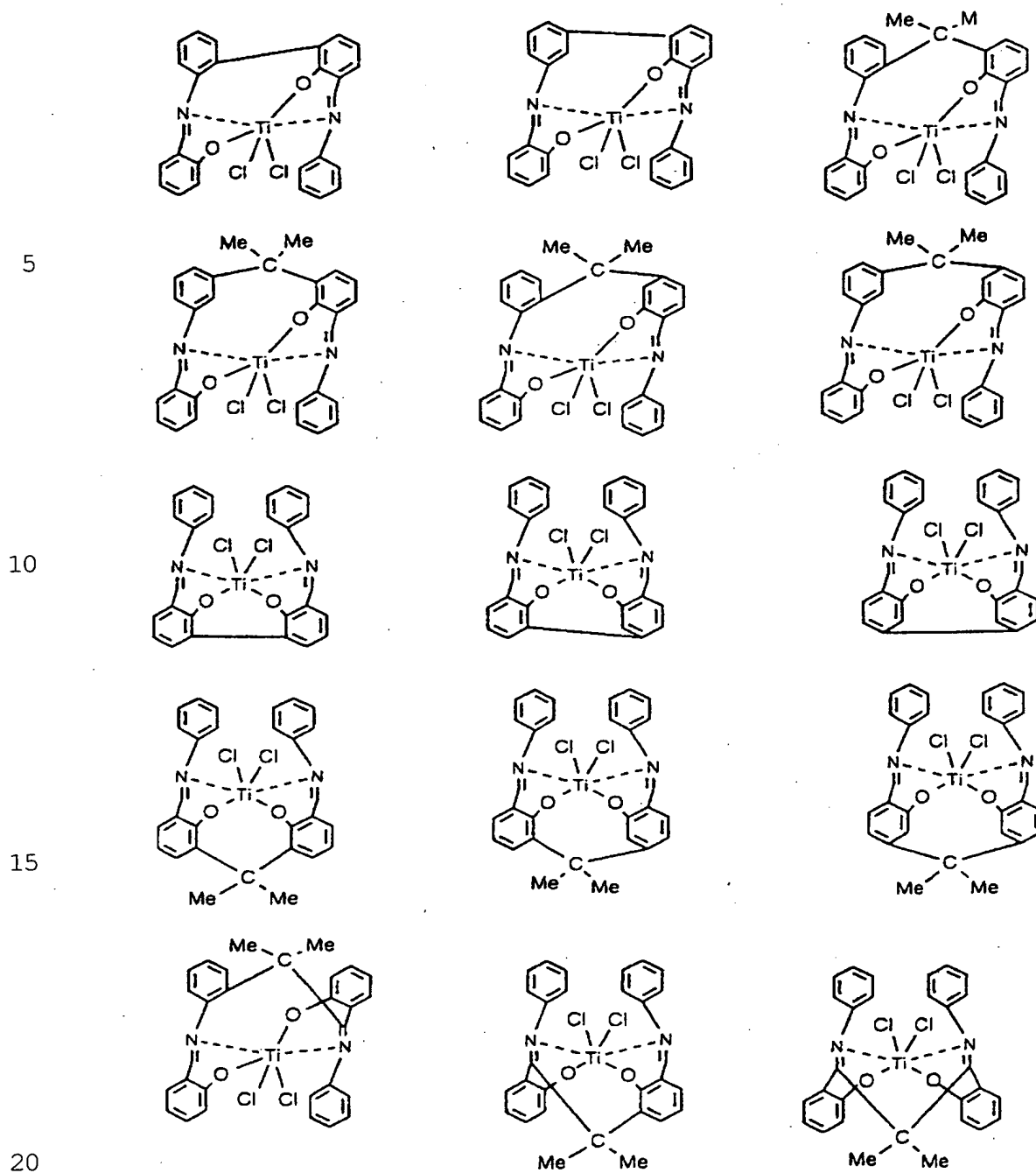


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[0081]



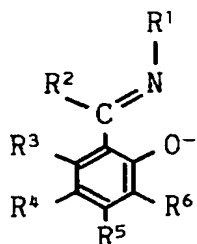




[0084]

Of the transition metal compounds, in anions of the transition metal compounds (following formula (III)):

[0085]



... (III)

[0086]

wherein R¹ to R⁶ are identical with R¹ to R⁶ in the formula (I), an energy difference between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) calculated by the Hamiltonian PM3 method of MOPAC VERSION 6.00 is preferably 8.50 or less, more preferably 8.00 or less.

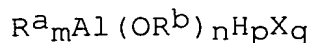
[0087]

15 (B-1) Organometallic compound

As the organometallic compound (B-1), the below-described organometallic compounds of metals of Group 1, Group 2, Group 12 and Group 13 of the periodic table are employable in the invention.

20 [0088]

(B-1a) Organoaluminum compound represented by the following formula:

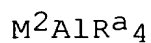


wherein R^a and R^b may be the same or different, and are each

a hydrocarbon group of 1 to 15 carbon atoms, preferably a hydrocarbon group of 1 to 4 carbon atoms; X is a halogen atom; and m, n, p and q are numbers satisfying the conditions of $0 < m \leq 3$, $0 \leq n < 3$, $0 \leq p < 3$, $0 \leq q < 3$ and $m+n+p+q = 3$.

5 [0089]

(B-1b) Alkyl complex compound of Group 1 metal and aluminum, that is represented by the following formula:



wherein M^2 is Li, Na or K; and R^a is a hydrocarbon group of 1 to 15 carbon atoms, preferably a hydrocarbon group of 1 to 4 carbon atoms.

[0090]

(B-1c) Dialkyl compound of Group 2 metal or Group 12 metal, that is represented by the following formula:

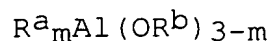


wherein R^a and R^b may be the same or different, and are each a hydrocarbon group of 1 to 15 carbon atoms, preferably a hydrocarbon group of 1 to 4 carbon atoms; and M^3 is Mg, Zn or Cd.

[0091]

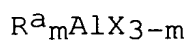
20 Examples of the organoaluminum compounds (B-1a) include the following compounds.

Organoaluminum compound represented by the following formula:



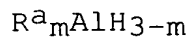
wherein R^a and R^b may be the same or different, and are each a hydrocarbon group of 1 to 15 carbon atoms, preferably a hydrocarbon group of 1 to 4 carbon atoms; and m is preferably a number satisfying the condition of $1.5 \leq m \leq 3$.

- 5 Organoaluminum compound represented by the following formula:



- wherein R^a is a hydrocarbon group of 1 to 15 carbon atoms, preferably a hydrocarbon group of 1 to 4 carbon atoms; X is
10 a halogen atom; and m is preferably a number satisfying the condition of $0 < m < 3$.

Organoaluminum compound represented by the following formula:



- 15 wherein R^a is a hydrocarbon group of 1 to 15 carbon atoms, preferably a hydrocarbon group of 1 to 4 carbon atoms; and m is preferably a number satisfying the condition of $2 \leq m < 3$.

Organoaluminum compound represented by the following formula:

- 20 $R^a_m Al (OR^b)_n X_q$

wherein R^a and R^b may be the same or different, and are each a hydrocarbon group of 1 to 15 carbon atoms, preferably a hydrocarbon group of 1 to 4 carbon atoms; X is a halogen atom; and m , n and q are numbers satisfying the conditions of $0 < m \leq 3$,

$0 \leq n < 3$, $0 \leq q < 3$ and $m+n+q = 3$.

[0092]

Particular examples of the organoaluminum compounds (B-1a) include:

5 tri-n-alkylaluminums, such as trimethylaluminum, triethylaluminum, tri-n-butylaluminum, tripropylaluminum, tripentylaluminum, trihexylaluminum, trioctylaluminum and tridecylaluminum;

branched-chain trialkylaluminums, such as
10 triisopropylaluminum, triisobutylaluminum, tri-sec-butylaluminum, tri-tert-butylaluminum, tri-2-methylbutylaluminum, tri-3-methylbutylaluminum, tri-2-methylpentylaluminum, tri-3-methylpentylaluminum, tri-4-methylpentylaluminum, tri-2-methylhexylaluminum,
15 tri-3-methylhexylaluminum and tri-2-ethylhexylaluminum;

tricycloalkylaluminums, such as tricyclohexylaluminum and tricyclooctylaluminum;

triarylaluminums, such as triphenylaluminum and tritolylaluminum;

20 dialkylaluminum hydrides, such as diisobutylaluminum hydride and diisobutylaluminum hydride;

trialkenylaluminums, such as triisoprenylaluminum represented by the formula $(i-C_4H_9)_xAl_y(C_5H_{10})_z$ (wherein x, y and z are positive numbers, and $z \geq 2x$);

alkylaluminum alkoxides, such as isobutylaluminum methoxide, isobutylaluminum ethoxide and isobutylaluminum isopropoxide;

dialkylaluminum alkoxides, such as dimethylaluminum methoxide, diethylaluminum ethoxide and dibutylaluminum butoxide;

5 alkylaluminum sesquialkoxides, such as ethylaluminum sesquiethoxide and butylaluminum sesquibutoxide;

partially alkoxyated alkylaluminums having an average composition represented by $R^{a}_{2.5}Al(OR^b)_{0.5}$;

10 dialkylaluminum aryloxides, such as diethylaluminum phenoxide, diethylaluminum(2,6-di-t-butyl-4-methylphenoxide), ethylaluminumbis(2,6-di-t-butyl-4-methylphenoxide), diisobutylaluminum(2,6-di-t-butyl-4-methylphenoxide) and isobutylaluminumbis(2,6-di-t-butyl-4-methylphenoxide);

15 dialkylaluminum halides, such as dimethylaluminum chloride, diethylaluminum chloride, dibutylaluminum chloride, diethylaluminum bromide and diisobutylaluminum chloride;

alkylaluminum sesquihalides, such as ethylaluminum sesquichloride, butylaluminum sesquichloride and ethylaluminum sesquibromide;

20 partially halogenated alkylaluminums, such as ethylaluminum dichloride, propylaluminum dichloride and butylaluminum dibromide;

dialkylaluminum hydrides, such as diethylaluminum hydride and dibutylaluminum hydride;

partially hydrogenated alkylaluminums, e.g.,
alkylaluminum dihydrides, such as ethylaluminum dihydride and
propylaluminum dihydride; and

partially alkoxylated and halogenated alkylaluminums,
5 such as ethylaluminum ethoxychloride, butylaluminum
butoxychloride and ethylaluminum ethoxybromide.

[0093]

Also employable are compounds analogous to the
organoaluminum compound (B-1a). For example, there can be
10 mentioned organoaluminum compounds wherein two or more
aluminum compounds are combined through a nitrogen atom, such
as $(C_2H_5)_2AlN(C_2H_5)Al(C_2H_5)_2$.

[0094]

Examples of the organoaluminum compounds (B-1b) include
15 $LiAl(C_2H_5)_4$ and $LiAl(C_7H_{15})_4$.

Further, other compounds such as methyllithium,
ethylolithium, propyllithium, butyllithium, methylmagnesium
bromide, methylmagnesium chloride, ethylmagnesium bromide,
ethylmagnesium chloride, propylmagnesium bromide,
20 propylmagnesium chloride, butylmagnesium bromide,
butylmagnesium chloride, dimethylmagnesium, diethylmagnesium,
dibutylmagnesium and butylethylmagnesium are also employable
as the organometallic compounds (B-1).

[0095]

Furthermore, combinations of compounds capable of producing the above-mentioned organoaluminum compounds in the polymerization system, e.g., a combination of halogenated aluminum and alkyl lithium and a combination of halogenated
5 aluminum and alkylmagnesium, are also employable.

[0096]

Of the organometallic compounds (B-1), the organoaluminum compounds are preferable.

The organometallic compounds (B-1) mentioned above can
10 be used singly or in combination of two or more kinds.

[0097]

(B-2) Organoaluminum oxy-compound

The organoaluminum oxy-compound (B-2) for use in the invention may be conventional aluminoxane or a benzene-
15 insoluble organoaluminum oxy-compound exemplified in Japanese Patent Laid-Open Publication No. 78687/1990.

[0098]

The conventional aluminoxane can be prepared by, for example, the following processes, and is generally obtained
20 as a hydrocarbon solvent solution.

(1) An organoaluminum compound such as trialkylaluminum is added to a hydrocarbon medium suspension of a compound containing adsorbed water or a salt containing water of crystallization, e.g., magnesium chloride hydrate,

copper sulfate hydrate, aluminum sulfate hydrate, nickel sulfate hydrate or cerous chloride hydrate, to allow the organoaluminum compound to react with the adsorbed water or the water of crystallization.

5 (2) Water, ice or water vapor is allowed to directly act on an organoaluminum compound such as trialkylaluminum in a medium such as benzene, toluene, ethyl ether or tetrahydrofuran.

10 (3) An organotin oxide such as dimethyltin oxide or dibutyltin oxide is allowed to react with an organoaluminum compound such as trialkylaluminum in a medium such as decane, benzene or toluene.

[0099]

15 The aluminosilane may contain a small amount of an organometallic component. Further, it is possible that the solvent or the unreacted organoaluminum compound is distilled off from the recovered solution of aluminosilane and the remainder is redissolved in a solvent or suspended in a poor solvent for aluminosilane.

20 [0100]

Examples of the organoaluminum compounds used for preparing the aluminosilane include the same organoaluminum compounds as described for the organoaluminum compound (B-1a).

[0101]

Of these, preferable are trialkylaluminums and tricycloalkylaluminums. Particularly preferable is trimethylaluminum.

The organoaluminum compounds can be used singly or in
5 combination of two or more kinds.

[0102]

Examples of the solvents used for preparing the aluminoxane include hydrocarbon solvents, e.g., aromatic hydrocarbons, such as benzene, toluene, xylene, cumene and
10 cymene; aliphatic hydrocarbons, such as pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons, such as cyclopentane, cyclohexane, cyclooctane and methylcyclopentane; petroleum fractions, such as gasoline, kerosine and gas oil; and halides of these aromatic,
15 aliphatic and alicyclic hydrocarbons, particularly chlorides and bromides thereof. Also employable are ethers such as ethyl ether and tetrahydrofuran. Of the solvents, particularly preferable are aromatic hydrocarbons and aliphatic hydrocarbons.

[0103]

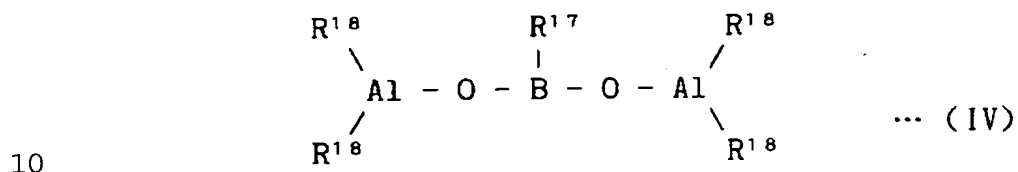
20 In the benzene-insoluble organoaluminum oxy-compound for use in the invention, the content of Al component which is soluble in benzene at 60 °C is usually not more than 10 %, preferably not more than 5 %, particularly preferably not more than 2 %, in terms of Al atom, and the benzene-insoluble

organoaluminum oxy-compound is insoluble or sparingly soluble in benzene.

[0104]

The organoaluminum oxy-compound used in the invention
5 may include an organoaluminum oxy-compound containing boron and represented by the following formula (IV):

[0105]



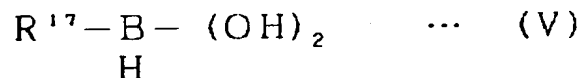
[0106]

wherein R^{17} is a hydrocarbon group of 1 to 10 carbon atoms;
and each R^{18} may be the same or different and is a hydrogen atom,
15 a halogen atom or a hydrocarbon group of 1 to 10 carbon atoms.

[0107]

The organoaluminum compound containing boron and
represented by the formula (IV) can be prepared by allowing
an alkylboronic acid represented by the following formula (V):

20 [0108]



[0109]

wherein R^{17} is the same group as described above, to react with an organoaluminum compound in an inert solvent under an inert gas atmosphere at a temperature of -80°C to room temperature for 1 minute to 24 hours:

5 [0110]

Examples of the alkylboronic acids represented by the formula (V) include methylboronic acid, ethylboronic acid, isopropylboronic acid, n-propylboronic acid, n-butylboronic acid, isobutylboronic acid, n-hexylboronic acid,
10 cyclohexylboronic acid, phenylboronic acid, 3,5-difluoroboronic acid, pentafluorophenylboronic acid and 3,5-bis(trifluoromethyl)phenylboronic acid. Of these, preferable are methylboronic acid, n-butylboronic acid, isobutylboronic acid, 3,5-difluorophenylboronic acid and
15 pentafluorophenylboronic acid. These are used singly or in combination of two or more kinds.

[0111]

Examples of the organoaluminum compounds to be reacted with the alkylboronic acid include the same organoaluminum
20 compounds as described for the organoaluminum compound (B-1a).

[0112]

Of these, preferable are trialkylaluminums and tricycloalkylaluminums. Particularly preferable are trimethylaluminum, triethylaluminum and triisobutylaluminum.

The organoaluminum compounds can be used singly or in combination of two or more kinds.

[0113]

The organoaluminum oxy-compounds (B-2) mentioned above
5 are used singly or in combination of two or more kinds.

(B-3) Compound which reacts with the transition metal compound to form ion pair

The compound (B-3) which reacts with the transition metal compound to form an ion pair (referred to as "ionizing ionic
10 compound" hereinafter), that is used in the invention, is a compound which reacts with the transition metal compound (A) to form an ion pair, and includes Lewis acid, an ionic compound, a borane compound and a carborane compound described in Japanese Patent Laid-Open Publications No. 501950/1989,
15 No. 502036/1989, No. 179005/1991, No. 179006/1991, No. 207703/1991 and No. 207704/1991, and U.S. Patent No. 5,321,106.

[0114]

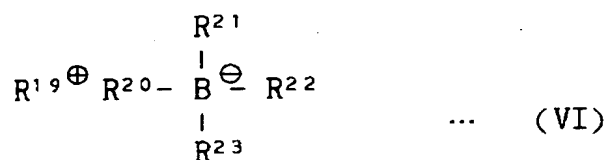
The Lewis acid is, for example, a compound represented by BR_3 (R is a phenyl group which may have a substituent such
20 as fluorine, methyl or trifluoromethyl, or a fluorine atom). Examples of such compounds include trifluoroboron, triphenylboron, tris(4-fluorophenyl)boron, tris(3,5-difluorophenyl)boron, tris(4-fluoromethylphenyl)boron, tris(pentafluorophenyl)boron, tris(p-tolyl)boron,

tris(o-tolyl)boron and tris(3,5-dimethylphenyl)boron.

[0115]

The ionic compound is, for example, a compound represented by the following formula (VI).

5 [0116]



[0117]

10 In the above formula, R^{19} is H^+ , carbonium cation, oxonium cation, ammonium cation, phosphonium cation, cycloheptyltrienyl cation, ferrocenium cation having a transition metal, or the like.

[0118]

15 R^{20} to R^{23} may be the same or different, and are each an organic group, preferably an aryl group or a substituted aryl group.

Examples of the carbonium cations include tri-substituted carbonium cations, such as triphenylcarbonium
20 cation, tri(methylphenyl)carbonium cation and tri(dimethylphenyl)carbonium cation.

[0119]

Examples of the ammonium cations include trialkylammonium cations, such as trimethylammonium cation,

triethylammonium cation, tripropylammonium cation,
tributylammonium cation and tri(n-butyl)ammonium cation;
N,N-dialkylanilinium cations, such as N,N-dimethylanilinium
cation, N,N-diethylanilinium cation and
5 N,N-2,4,6-pentamethylanilinium cation; and
dialkylammonium cations, such as di(isopropyl)ammonium cation
and dicyclohexylammonium cation.

[0120]

Examples of the phosphonium cations include
10 triarylphosphonium cations, such as triphenylphosphonium
cation, tri(methylphenyl)phosphonium cation and
tri(dimethylphenyl)phosphonium cation.

[0121]

R¹⁹ is preferably carbonium cation or ammonium cation,
15 particularly preferably triphenylcarbonium cation,
N,N-dimethylanilinium cation or N,N-diethylanilinium cation.

[0122]

Also available as the ionic compound is a
trialkyl-substituted ammonium salt, a N,N-dialkylanilinium salt,
20 a dialkylammonium salt and a triarylphosphonium salt.

[0123]

Examples of the trialkyl-substituted ammonium salts
include triethylammoniumtetra(phenyl)boron,
tripropylammoniumtetra(phenyl)boron,

tri(n-butyl) ammoniumtetra(phenyl)boron,
trimethylammoniumtetra(p-tolyl)boron,
trimethylammoniumtetra(o-tolyl)boron,
tri(n-butyl) ammoniumtetra(pentafluorophenyl)boron,
5 tripropylammoniumtetra(o,p-dimethylphenyl)boron,
tri(n-butyl) ammoniumtetra(m,m-dimethylphenyl)boron,
tri(n-butyl) ammoniumtetra(p-trifluoromethylphenyl)boron,
tri(n-butyl) ammoniumtetra(3,5-ditrifluoromethylphenyl)boron
and tri(n-butyl) ammoniumtetra(o-tolyl)boron.

10 [0124]

Examples of the N,N-dialkylanilinium salts include
N,N-dimethylaniliniumtetra(phenyl)boron,
N,N-diethylaniliniumtetra(phenyl)boron and
N,N-2,4,6-pentamethylaniliniumtetra(phenyl)boron.

15 [0125]

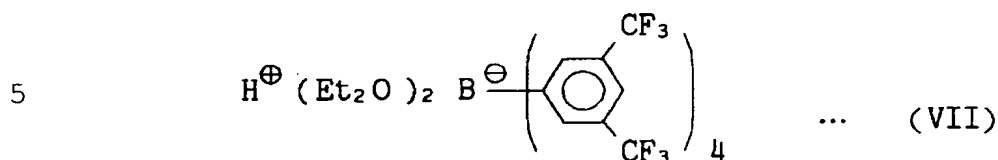
Examples of the dialkylammonium salts include
di(1-propyl) ammoniumtetra(pentafluorophenyl)boron and
dicyclohexylammoniumtetra(phenyl)boron.

[0126]

20 Further employable as the ionic compound is
triphenylcarbeniumtetrakis(pentafluorophenyl)borate,
N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate,
ferroceniumtetra(pentafluorophenyl)borate,
triphenylcarbeniumpentaphenylcyclopentadienyl complex,

N,N-diethylaniliniumpentaphenylcyclopentadienyl complex or a boron compound represented by the following formula (VII) or (VIII).

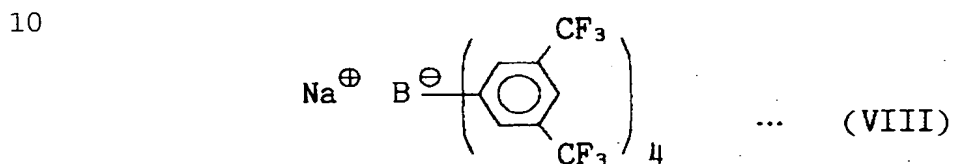
[0127]



[0128]

In the above formula, Et is an ethyl group.

[0129]



[0130]

Examples of the borane compounds include:

- 15 decaborane(14); salts of anions, such as
 bis[tri(n-butyl)ammonium]nonaborate,
 bis[tri(n-butyl)ammonium]decaborate,
 bis[tri(n-butyl)ammonium]undecaborate,
 bis[tri(n-butyl)ammonium]dodecaborate,
 20 bis[tri(n-butyl)ammonium]decachlorodecaborate and
 bis[tri(n-butyl)ammonium]dodecachlorododecaborate; and
 salts of metallic borane anions, such as
 tri(n-butyl)ammoniumbis(dodecahydridedodecaborate)cobaltate(III)
 and bis[tri(n-butyl)ammonium]bis(dodecahydridedodecaborate)

nickelate(III).

[0131]

Examples of the carborane compounds include:

salts of anions, such as 4-carbanonaborane(14),

- 5 1,3-dicarbanonaborane(13), 6,9-dicarbadekaborane(14),
dodecahydride-1-phenyl-1,3-dicarbanonaborane,
dodecahydride-1-methyl-1,3-dicarbanonaborane,
undecahydride-1,3-dimethyl-1,3-dicarbanonaborane,
7,8-dicarbadekaborane(13), 2,7-dicarbadekaborane(13),
10 undecahydride-7,8-dimethyl-7,8-dicarbadekaborane,
dodecahydride-11-methyl-2,7-dicarbadekaborane,
tri(n-butyl) ammonium-1-carbadekaborate,
tri(n-butyl) ammonium-1-carbadekaborate,
tri(n-butyl) ammonium-1-carbadodekaborate,
15 tri(n-butyl) ammonium-1-trimethylsilyl-1-carbadekaborate,
tri(n-butyl) ammoniumbromo-1-carbadodekaborate,
tri(n-butyl) ammonium-6-carbadekaborate(14),
tri(n-butyl) ammonium-6-carbadekaborate(12),
tri(n-butyl) ammonium-7-carbadekaborate(13),
20 tri(n-butyl) ammonium-7,8-dicarbadekaborate(12),
tri(n-butyl) ammonium-2,9-dicarbadekaborate(12),
tri(n-butyl) ammoniumdodecahydride-8-methyl-7,9-dicarbadekaborate,
tri(n-butyl) ammoniumundecahydride-8-ethyl-7,9-dicarbadekaborate,
tri(n-butyl) ammoniumundecahydride-8-butyl-7,9-dicarbadekaborate,

tri(n-butyl)ammoniumundecahydride-8-allyl-7,9-dicarbaundecaborate,
tri(n-butyl)ammoniumundecahydride-9-trimethylsilyl-7,8-
dicarbaundecaborate and tri(n-butyl)ammoniumundecahydride-
4,6-dibromo-7-carbaundecaborate; and

5 salts of metallic carborane anions, such as

tri(n-butyl)ammoniumbis(nonahydride-1,3-dicarbonoborate)
cobaltate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-
dicarbaundecaborate)ferrate(III), tri(n-butyl)ammoniumbis
(undecahydride-7,8-dicarbaundecaborate)cobaltate(III),

10 tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)
nickelate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-
dicarbaundecaborate)cuprate(III), tri(n-butyl)ammoniumbis
(undecahydride-7,8-dicarbaundecaborate)aurate(III),

tri(n-butyl)ammoniumbis(nonahydride-7,8-dimethyl-7,8-
15 dicarbaundecaborate)ferrate(III), tri(n-butyl)ammoniumbis
(nonahydride-7,8-dimethyl-7,8-dicarbaundecaborate)chromate(III),
tri(n-butyl)ammoniumbis(tribromooctahydride-7,8-
dicarbaundecaborate)cobaltate(III), tris[tri(n-butyl)ammonium]bis
(undecahydride-7-carbaundecaborate)chromate(III),

20 bis[tri(n-butyl)ammonium]bis(undecahydride-7-carbaundecaborate)
manganate(IV), bis[tri(n-butyl)ammonium]bis(undecahydride-
7-carbaundecaborate)cobaltate(III) and bis[tri(n-butyl)ammonium]bis
(undecahydride-7-carbaundecaborate)nickelate(IV).

[0132]

The ionizing ionic compounds (B-3) mentioned above can be used singly or in combination of two or more kinds.

In the olefin polymerization catalyst of the invention, the below-described fine particle carrier (C) can be used if
5 necessary, in addition to the above-mentioned transition metal compound (A) and at least one compound (B) selected from the organometallic compound (B-1), the organoaluminum oxy-
compound (B-2) and the ionized ionic compound (B-3).

[0133]

10 (C) Fine particle carrier

The fine particle carrier (C) for use in the invention is an inorganic or organic compound in the form of granular or fine particle solid having a particle diameter of 10 to 300 μm , preferably 20 to 200 μm . As the inorganic compound, porous
15 oxide is preferable. Examples of the porous oxides include SiO_2 , Al_2O_3 , MgO , ZrO , TiO_2 , B_2O_3 , CaO , ZnO , BaO , ThO_2 ; and mixtures containing these oxides, such as $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-V}_2\text{O}_5$, $\text{SiO}_2\text{-Cr}_2\text{O}_3$ and $\text{SiO}_2\text{-TiO}_2\text{-MgO}$. Of these, preferable are compounds containing at least one selected from
20 the group of SiO_2 and Al_2O_3 as the main component.

[0134]

The inorganic oxides may contain a small amount of carbonate, sulfate, nitrate or oxide component, such as Na_2CO_3 , K_2CO_3 , CaCO_3 , MgCO_3 , Na_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, BaSO_4 , KNO_3 , $\text{Mg}(\text{NO}_3)_2$,

$\text{Al}(\text{NO}_3)_3$, Na_2O , K_2O or Li_2O .

[0135]

Though the fine particle carrier (C) differ in their properties depending on the type and the preparation process thereof, the carrier preferably used in the invention has a specific surface area of 50 to 1,000 m^2/g , preferably 100 to 700 m^2/g , and a pore volume of 0.3 to 2.5 cm^3/g . The carrier can be used after calcined at 100 to 1,000 $^\circ\text{C}$, preferably 150 to 700 $^\circ\text{C}$, if desired.

10 [0136]

The fine particle carrier (C) is, for example, a granular or particle solid of organic compound having a particle diameter of 10 to 300 μm . Examples of such organic compounds include (co)polymers produced using, as main components, α -olefins of 2 to 14 carbon atoms such as ethylene, propylene, 1-butene and 4-methyl-1-pentene, and (co)polymers produced using, as a main component, vinylcyclohexane or styrene.

[0137]

The olefin polymerization catalyst according to the invention comprises the above-mentioned transition metal compound (A) and at least one compound (B) selected from the organometallic compound (B-1), the organoaluminum oxy-compound (B-2) and the ionized ionic compound (B-3) and optionally the fine particle carrier (C).

[0138]

In the polymerization, the components can be used in any way and in any order. Some examples of the processes are given below.

- (1) The component (A) and at least one component (B) selected
5 from the organometallic compound (B-1), the organoaluminum oxy-compound (B-2) and the ionized ionic compound (B-3) (referred to simply as "component (B)" hereinafter) are fed to the polymerization reactor in an arbitrary order.
- (2) A catalyst previously contacted the component (A) with
10 the component (B) is fed to the polymerization reactor.
- (3) A catalyst component previously contacted the component (A) with the component (B), and the component (B) are fed to the polymerization reactor in an arbitrary order. In this case, the components (B) may be the same or different.
- 15 (4) A catalyst component wherein the component (A) is supported on the fine particle carrier (C), and the component (B) are fed to the polymerization reactor in an arbitrary order.
- (5) A catalyst wherein the component (A) and the component (B) are supported on the fine particle carrier (C) is fed to
20 the polymerization reactor.
- (6) A catalyst component wherein the component (A) and the component (B) are supported on the fine particle carrier (C), and the component (B) are fed to the polymerization reactor in an arbitrary order. In this case, the components (B) may

be the same or different.

(7) A catalyst component wherein the component (B) is supported on the fine particle carrier (C), and the component (A) are fed to the polymerization reactor in an arbitrary order.

5 (8) A catalyst component wherein the component (B) is supported on the fine particle carrier (C), the component (A) and the component (B) are fed to the polymerization reactor in an arbitrary order. In this case, the components (B) may be the same or different.

10 [0139]

For the solid catalyst component wherein the component (A) and the component (B) are supported on the fine particle carrier (C), an olefin may be prepolymerized.

15 In the process for olefin polymerization according to the invention, an olefin is polymerized or copolymerized in the presence of the above-described olefin polymerization catalyst to obtain an olefin polymer.

[0140]

20 In the present invention, the polymerization can be carried out as any of liquid phase polymerization, such as solution polymerization or suspension polymerization, and gas phase polymerization.

Examples of the inert hydrocarbon media used in the liquid phase polymerization include aliphatic hydrocarbons,

such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane and kerosine; alicyclic hydrocarbons, such as cyclopentane, cyclohexane and methylcyclopentane; aromatic hydrocarbons, such as benzene, toluene and xylene; halogenated hydrocarbons, such as ethylene chloride, chlorobenzene and dichloromethane; and mixtures of these hydrocarbons. The olefin itself can be used as the solvent.

[0141]

In the polymerization of an olefin using the olefin polymerization catalyst, the component (A) is used in an amount of usually 10^{-8} to 10^{-2} mol, preferably 10^{-7} to 10^{-3} mol, based on 1 liter of the reaction volume. In the present invention, an olefin can be polymerized with high polymerization activities, even if the component (A) is used in a relatively low concentration.

[0142]

The component (B-1) is used in such an amount that the molar ratio of the component (B-1) to the transition metal atom (M) in the component (A) $((B-1)/(M))$ becomes usually 0.01 to 100,000, preferably 0.05 to 50,000. The component (B-2) is used in such an amount that the molar ratio of the aluminum atom in the component (B-2) to the transition metal atom (M) in the component (A) $((B-2)/(M))$ becomes usually 10 to 500,000, preferably 20 to 100,000. The component (B-3) is used in such

an amount that the molar ratio of the component (B-3) to the transition metal atom (M) in the component (A) $((B-3)/(M))$ becomes usually 1 to 10, preferably 1 to 5.

[0143]

5 The temperature for the olefin polymerization using the olefin polymerization catalyst is in the range of usually -50 to 200 °C, preferably 0 to 170 °C. The polymerization pressure is in the range of usually atmospheric pressure to 100 kg/cm², preferably atmospheric pressure to 50 kg/cm². The
10 polymerization reaction can be carried out by any of batchwise, semi-continuous and continuous processes. The polymerization can be conducted in two or more stages under different reaction conditions.

[0144]

15 The molecular weight of the resulting polymer can be adjusted by allowing hydrogen to exist in the polymerization system or by varying the polymerization temperature.

Further, the molecular weight can be adjusted also by using the component (B) of different type.

20 [0145]

Examples of the olefins which can be polymerized using the olefin polymerization catalyst include:

straight-chain or branched α -olefins of 2 to 30, such as ethylene, propylene, 1-butene, 1-pentene, 3-methyl-1-butene,

1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene; and

cycloolefins of 3 to 20, such as cyclopentene, 5 cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene and 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene.

polar monomers, such as α,β -unsaturated carboxylic acids, e.g., acrylic acid, methacrylic acid, fumaric acid, maleic 10 anhydride, itaconic acid, itaconic anhydride and bicyclo(2,2,1)-5-heptene-2,3-dicarboxylic acid, and metallic salts of these acids, e.g., sodium salts, potassium salts, lithium salts, zinc salts, magnesium salts and calcium salts; α,β -unsaturated carboxylic esters, such as methyl acrylate, 15 ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate and isobutyl methacrylate; vinyl esters, such as 20 vinyl acetate, vinyl propionate, vinyl caproate, vinyl caprate, vinyl laurate, vinyl stearate and vinyl trifluoroacetate; and unsaturated glycidyl esters, such as glycidyl acrylate, glycidyl methacrylate and monoglycidyl itaconate. Furthermore, styrene, vinylcyclohexane, diene

and the like are also employable. The diene and the polyene are cyclic or chain compounds having 4 to 20 carbon atoms and having two or more double bonds. Examples of such compounds include butadiene, isoprene, 4-methyl-1,3-pentadiene,

5 1,3-pentadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene, 1,3-hexadiene, 1,3-octadiene, 1,4-octadiene, 1,5-octadiene, 1,6-octadiene, 1,7-octadiene, ethylidene norbornene, vinyl norbornene and dicyclopentadiene.

[0146]

10 The olefin polymerization catalyst of the invention exhibits high polymerization activities, and by the use of the catalyst, polymers of narrow molecular weight distribution can be obtained. When two or more kinds of olefins are copolymerized, olefin copolymers of narrow composition
15 distribution can be obtained.

[0147]

The olefin polymerization catalyst of the invention can be used also for the copolymerization of an α -olefin and a conjugated diene.

20 Examples of the α -olefins used herein include the same straight-chain or branched α -olefins of 2 to 20 as described above. Of these, preferable are ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene and 1-octene. Particularly preferable are ethylene and propylene.

These α -olefins can be used singly or in combination or two or more kinds.

[0148]

Examples of the conjugated dienes include aliphatic
5 conjugated dienes of 4 to 30, preferably 4 to 20 carbon atoms, such as 1,3-butadiene, isoprene, chloroprene, 1,3-cyclohexadiene, 1,3-pentadiene, 4-methyl-1,3-pentadiene, 1,3-hexadiene and 1,3-octadiene. These conjugated dienes can be used singly or in combination of two or more kinds.

10 [0149]

In the present invention, in the copolymerization of the α -olefin and the conjugated diene, non-conjugated diene or polyene is further employable, and examples thereof include 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene, 1,4-octadiene,
15 1,5-octadiene, 1,6-octadiene, 1,7-octadiene, ethylidene norbornene, vinyl norbornene, dicyclopentadiene or the like.

[0150]

It is desired that the α -olefin/conjugated diene copolymer according to the invention comprises 1 to 99.9 % by
20 mol of constituent units derived from an α -olefin and 99 to 0.1 % by mol of constituent units derived from a conjugated diene, and preferably comprises 50 to 99.9 % by mol of constituent units derived from an α -olefin and 50 to 0.1 % by mol of constituent units derived from a conjugated diene.

[0151]

In the polymer chain of the α -olefin/conjugated diene copolymer of the invention, the content of 1,2-cyclopentane skeleton derived from the conjugated diene is not more than 1 %
5 by mol, preferably such a content that the 1,2-cyclopentadiene skeleton can be regarded to be substantially not contained (i.e., less than 0.1 % by mol). When the content of the 1,2-cyclopentane skeleton is less than 0.1 % by mol, the content is regarded to be lower than the detection limit and is not
10 introduced into the calculation of all the conjugated diene units.

[0152]

Further, in the polymer chain of the α -olefin/conjugated diene copolymer of the invention, the proportion of the
15 1,2-cyclopentane skeleton to all the diene units is not more than 20 %, preferably not more than 10 %. The proportions of other insertions of the dienes (e.g., 1,4-cis, 1,4-trans, 1,2-vinyl) in the α -olefin/conjugated diene copolymer are arbitrary. The proportions can be determined by ^{13}C -NMR and
20 ^1H -NMR in accordance with the method described in "Die Makromolekulare Chemie", volume 192, p. 2591 (1991).

[0153]

The α -olefin/conjugated diene copolymer has a molecular weight distribution (M_w/M_n) of not more than 3.5 and has a

uniform composition distribution. The weight average molecular weight (Mw) of the copolymer is not less than 1,000, preferably not less than 5,000.

[0154]

5 [Effect of the invention]

The olefin polymerization catalyst according to the invention has high polymerization activities on olefins.

[0155]

10 In the process for olefin polymerization according to the invention, an olefin (co)polymer of narrow molecular distribution can be produced with high polymerization activities. When an α -olefin and a conjugated diene are copolymerized, a copolymer containing almost no 1,2-cyclopentane skeleton in the polymer chain can be produced.

15 [0156]

The α -olefin/conjugated diene copolymer according to the invention has a narrow molecular weight distribution and contains almost no cyclopentane skeleton in the polymer chain.

[0157]

20 [Example]

The present invention is further described with reference to the following examples, but it should be construed that the invention is in no way limited to those examples.

[0158]

Further, the intrinsic viscosity $[\eta]$ was measured in decalin at 135 °C and expressed in dl/g.

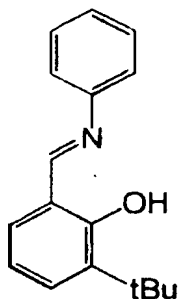
[0159]

[Synthesis Example 1]

5 Synthesis of ligand (L1)

To a 100 ml reactor thoroughly purged with nitrogen, 40 ml of ethanol, 0.71 g (7.62 mmol) of aniline and 1.35 g (7.58 mmol) of 3-t-butylsalicylaldehyde were introduced, and they were stirred at room temperature for 24 hours. The reaction
10 solution was concentrated under reduced pressure to remove the solvent. Then, 40 ml of ethanol was added again, and the mixture was stirred at room temperature for 12 hours. The reaction solution was concentrated under reduced pressure to obtain 1.83 g (yield: 95 %) of a compound represented by the
15 following formula (L1) as an orange oil. The energy difference between HOMO and LUMO calculated by the Hamiltonian PM3 method of MOPAC VERSION 6.00 in a state of anionizing this compound was 6.38 eV.

[0160]



L1

[0161]

Synthesis of compound 1

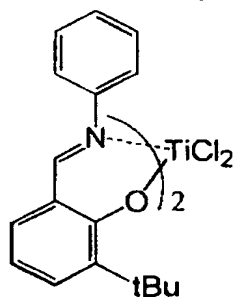
10 In a 200 ml reactor thoroughly purged with nitrogen, the compound (L1) obtained above was used to conduct a complex synthesis. 0.60 g (2.37 mmol) of compound L1 and 50 ml of absolute diethyl ether were introduced thereto, and they were cooled to -78 °C and stirred. After 1.53 ml of n-butyllithium

15 (1.63N n-hexane solution, 2.49 mmol) was dropped over a period of 5 minutes, the temperature was slowly raised to room temperature, and stirring was continued for 4 hours at room temperature. After the solution was slowly dropped to a mixture of 2.4 ml of TiCl₄ (0.5 mmol/ml decane solution, 1.20

20 mmol) and 40 ml of diethyl ether which had been been cooled to -78 °C, the temperature was slowly raised to room temperature. After stirring for 4 hours at room temperature, the reaction solution was filtered with a glass filter, and the resulting solid was washed with 100 ml of absolute methylene chloride

to remove insolubles. The resulting methylene chloride solution was concentrated under reduced pressure, and the solid precipitated was washed with 100 ml of absolute hexane. The deposited solid was dried under reduced pressure to obtain 0.20 g (yield: 27 %) of compound 1 represented by the following formula as orange crystals. The result of FD-mass spectrometry of compound 1 is 622 (M^+).

[0162]



Compound 1

15 [0163]

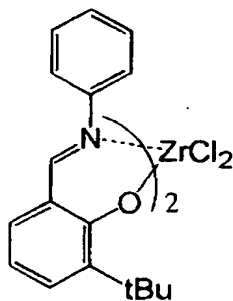
[Synthesis Example 2]

Synthesis of compound 2

To a 200 ml reactor thoroughly purged with nitrogen, 0.50 g (1.97 mmol) of compound (L1) obtained in the Synthesis Example 1 and 50 ml of absolute diethyl ether were introduced, and they were cooled to -78 °C and stirred. After 1.28 ml of n-butyllithium (1.63N n-hexane solution, 2.09 mmol) was dropped over a period of 5 minutes, the temperature was slowly raised to room temperature. The solution was stirred for 4

hours at room temperature, and then was cooled to -78°C again .
After 0.37g (0.98 mmol) of $\text{ZrCl}_4 \cdot \text{THF}_2$ was slowly added, the
reaction solution was slowly raised to room temperature.
After the solution was stirred for 2 hours at room temperature,
5 50 mL of absolute tetrahydrofuran was added, and the mixture
was stirred for 3 hours under reflux. The reaction solution
was concentrated under reduced pressure, and the solid
precipitated was washed with 100 mL of absolute diethyl ether.
The resulting solid was washed with 100 ml of absolute methylene
10 chloride to remove insolubles. The resulting methylene
chloride solution was concentrated under reduced pressure, and
the solid precipitated was washed with 50 ml of mixture of
absolute diethyl ether and absolute hexane (absolute diethyl
ether : absolute hexane = 1:1). The resulting solid was dried
15 under reduced pressure to obtain 0.38 g (yield: 58 %) of
compound 2 represented by the following formula as brownish
green crystals. The result of FD-mass spectrometry of
compound 2 is 664 (M^+).

[0164]



Compound 2

[0165]

[Synthesis Example 3]

Synthesis of compound 3

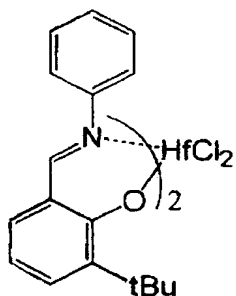
10 To a 200 ml reactor thoroughly purged with nitrogen, 0.50 g (1.9 mmol) of compound (L1) obtained in the Synthesis Example 1 and 50 ml of absolute diethyl ether were introduced, and they were cooled to -78 °C and stirred. After 1.28 ml of n-butyllithium (1.63N n-hexane solution, 2.09 mmol) was

15 dropped over a period of 5 minutes, the temperature was slowly raised to room temperature, and stirring was continued for 4 hours at room temperature. After the solution was slowly dropped to a mixture of 0.39 g of HfCl₄ (1.2 mmol) in 10 ml of THF which had been cooled to -78 °C, the temperature was

20 slowly raised to room temperature. The reaction solution was concentrated under reduced pressure, and the solid precipitated was washed with 20 ml of absolute diethyl ether. The obtained solid was washed with 10 ml of absolute methylene chloride to remove insolubles. The resulting methylene

chloride solution was concentrated under reduced pressure, and the solid precipitated was washed with 10 ml of mixture of absolute diethyl ether and absolute hexane (absolute diethyl ether : absolute hexane = 1:1). The resulting solid was dried under reduced pressure to obtain 0.30 g (yield: 33 %) of compound 3 represented by the following formula as fluorescent yellow crystals. The result of FD-mass spectrometry of compound 3 is 754 (M^+).

[0166]



Compound 3

[0167]

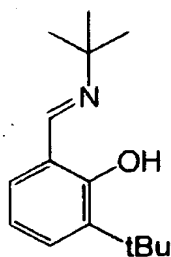
[Synthesis Example 4]

Synthesis of ligand L4

In the same conditions as those in the Synthesis Example 1, 0.90 g (12.0 mmol) of t-butylamine and 1.78 g (10.0 mmol) of 3-t-butylsalicylaldehyde were reacted to obtain 2.17 g (yield: 93%) of a compound represented by the following formula (L4) as a fluorescent yellow oil. The energy difference between HOMO and LUMO in a state of anionizing the compound (L4)

calculated by the Hamiltonian PM3 method of MOPAC VERSION 6.00 was 7.44 eV.

[0168]



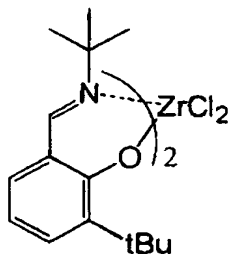
L4

10 [0169]

Synthesis of compound 4

Synthesis was conducted using 0.77 g (3.3 mmol) of compound (L4) obtained above and 0.38 g (1.65 mmol) of ZrCl₄ in the similar manner as in the Synthesis Example 2 to obtain 0.31 g (yield: 30 %) of other compound 4. The result of FD-mass spectrometry of compound 4 is 626(M⁺).

[0170]



Compound 4

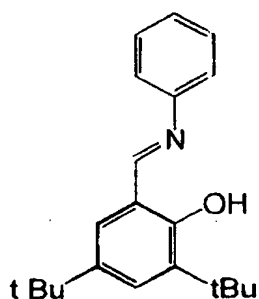
[0171]

[Synthesis Example 5]

Synthesis of ligand L5

In the same conditions as those in the Synthesis Example 1, 1.03 g (11.0 mmol) of aniline and 2.37 g (10.0 mmol) of 3,5-di-*t*-butylsalicylaldehyde were reacted to obtain 2.47 g (yield: 80 %) of a compound represented by the following formula (L5) as a yellow orange powder. The energy difference between HOMO and LUMO in a state of anionizing the compound (L5) calculated by the Hamiltonian PM3 method of MOPAC VERSION 6.00 was 6.36 eV.

[0172]

**L5**

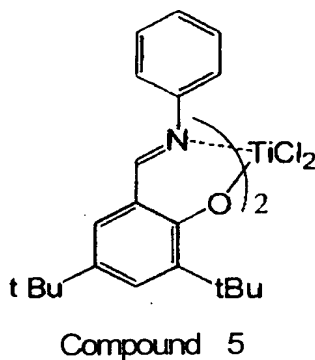
[0173]

Synthesis of compound 5

Synthesis was conducted using 0.93 g (3.0 mmol) of compound (L5) obtained above and 3.0 mL of TiCl_4 solution (0.5 mmol/mL heptane solution, 1.5 mmol) in the similar manner as in the Synthesis Example 1 to obtain 0.41 g (yield: 37 %) of compound 5 as brown powder. The result of FD-mass spectrometry

of compound 5 is 734 (M^+).

[0174]



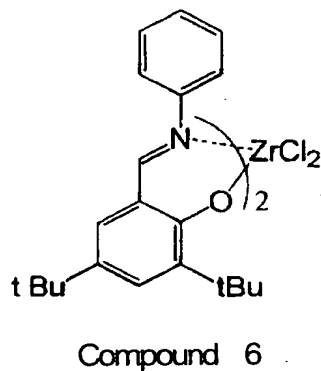
[0175]

10 [Synthesis Example 6]

Synthesis of compound 6

Synthesis was conducted using 0.93 g (3.0 mmol) of compound (L5) obtained in the Synthesis Example 5 and 0.35 g (1.5 mmol) of $ZrCl_4$ solution in the similar manner as in the Synthesis Example 2 to obtain 0.71 g (yield: 61 %) of an other compound 6. The result of FD-mass spectrometry of compound 6 is 779 (M^+).

[0176]



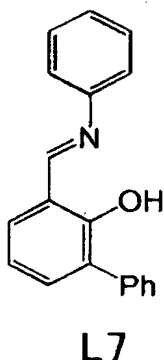
[0177]

[Synthesis Example 7]

Synthesis of ligand L7

In the same conditions as those in the Synthesis Example 1,
5 1.34 g (14.4 mmol) of aniline and 3.00 g (14.3 mmol) of
3-phenylsalicylaldehyde were reacted to obtain 3.35 g (yield:
85 %) of a compound represented by the following formula (L7)
as orange needle crystals. The energy difference between HOMO
and LUMO in a state of anionizing the compound (L7) calculated by
10 the Hamiltonian PM3 method of MOPAC VERSION 6.00 was 6.26 eV.

[0178]



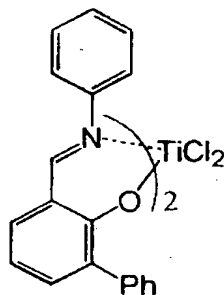
[0179]

20 Synthesis of compound 7

Synthesis was conducted using 1.00 g (3.7 mmol) of
compound (L7) obtained above and 3.7 mL of TiCl_4 solution (0.5
mmol/mL heptane solution, 1.65 mmol) in the similar manner as
in the Synthesis Example 1 to obtain 0.95 g (yield: 78 %) of

compound 7 as a brown powder. The result of FD-mass spectrometry of compound 7 is 662(M⁺).

[0180]



Compound 7

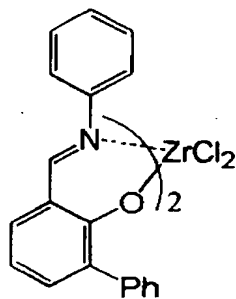
10 [0181]

[Synthesis Example 8]

Synthesis of compound 8

Synthesis was conducted using 1.00 g (3.7 mmol) of compound (L7) obtained in the Synthesis Example 7 and 0.43 g (1.8 mmol) of ZrCl₄ in the similar manner as in the Synthesis Example 2 to obtain 0.94 g (yield: 73 %) of compound 8 as a yellow green powder. The result of FD-mass spectrometry of compound 8 is 704(M⁺).

[0182]



Compound 8

[0183]

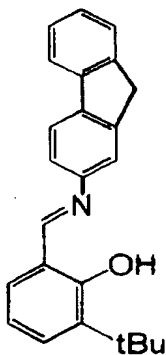
[Synthesis Example 9]

Synthesis of ligand L9

10 In the same conditions as those in the Synthesis Example 1, 2.03 g (11.2 mmol) of 2-aminofluorene and 1.78 g (10.0 mmol) of 3-phenylsalicylaldehyde were reacted to obtain 2.78 g (yield: 93 %) of a compound represented by the following formula (L9) as a yellow powder. The energy difference between HOMO

15 and LUMO in a state of anionizing the compound (L9) calculated by the Hamiltonian PM3 method of MOPAC VERSION 6.00 was 5.66 eV.

[0184]



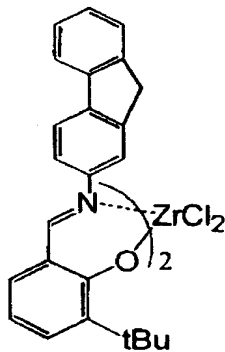
L9

[0185]

Synthesis of compound 9

Synthesis was conducted using 1.00 g (2.9 mmol) of compound (L9) obtained above and 0.34 g (1.45 mmol) of ZrCl_4 in the similar manner as in the Synthesis Example 2 to obtain 1.02 g (yield: 83 %) of an other compound 9. The result of FD-mass spectrometry of compound 9 is 842(M^+).

[0186]



Compound 9

[0187]

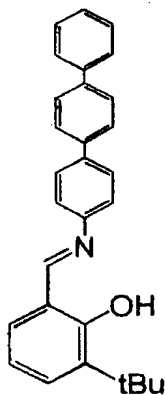
[Synthesis Example 10]

Synthesis of ligand 10

1.00 g (3.9 mmol) of 4-amino-p-terphenyl and 0.65 g (3.6 mmol) of 3-t-butylsalicylaldehyde were reacted in toluene under reflux. The resulting solid was recrystallized with methanol to obtain 1.29 g (yield: 88 %) of a compound represented by the following formula L10 as a yellow powder. The energy difference between HOMO and LUMO in a state of

anionizing the compound (L10) calculated by the Hamiltonian PM3 method of MOPAC VERSION 6.00 was 4.82 eV.

[0188]



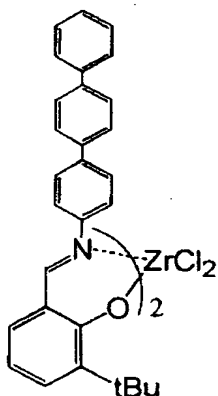
L10

[0189]

Synthesis of compound 10

Synthesis was conducted using 0.50 g (1.2 mmol) of compound (L10) obtained above and 0.14 g (0.6 mmol) of ZrCl_4 in the similar manner as in the Synthesis Example 2 to obtain 0.19 g (yield: 32 %) of a light yellow compound 10. The result of FD-mass spectrometry of compound 10 is 970 (M^+).

[0190]



Compound 10

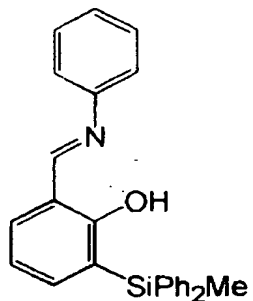
[0191]

[Synthesis Example 11]

10 Synthesis of ligand L11

In the same conditions as those in the Synthesis Example 1, 0.21 g (2.2 mmol) of aniline and 0.64 g (2.0 mmol) of 3-diphenylmethyilsilyl-salicylaldehyde were reacted to obtain 0.77 g (yield: 98 %) of a compound represented by the following
15 formula (L11) as a fluorescent yellow oil. The energy difference between HOMO and LUMO in a state of anionizing the compound (L11) calculated by the Hamiltonian PM3 method of MOPAC VERSION 6.00 was 6.43 eV.

[0192]



5

L11

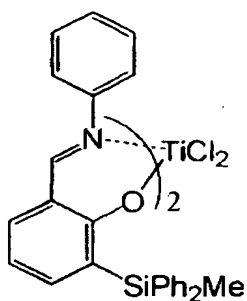
[0193]

Synthesis of compound 11

10 Synthesis was conducted using 0.40 g (1.0 mmol) of compound (L11) obtained above and 1 mL of TiCl_4 solution (0.5 mmol/mL heptane solution, 0.5 mmol) in the similar manner as in the Synthesis Example 1 to obtain 0.19 g (yield: 42 %) of compound 11 as a red brown powder. The result of FD-mass

15 spectrometry of compound 11 is 900 (M^+).

[0194]



20

Compound 11

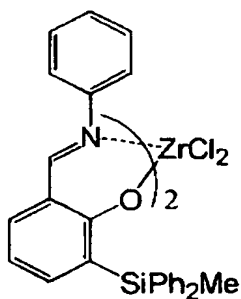
[0195]

[Synthesis Example 12]

Synthesis of compound 12

Synthesis was conducted using 0.40 g (1.0 mmol) of compound (L11) obtained in the Synthesis Example 11 and 0.12 g (0.5 mmol) of ZrCl_4 in the similar manner as in the Synthesis Example 2 to obtain 0.21 g (yield: 42 %) of compound 11 as a grayish white powder. The result of FD-mass spectrometry of compound 12 is 944 (M^+).

[0196]

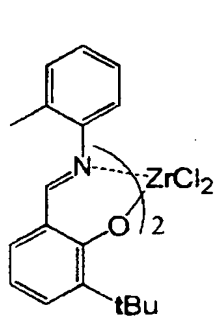


Compound 12

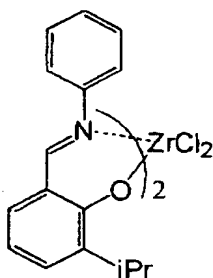
[0197]

Compounds 13 to 17 were synthesized in the similar manner.

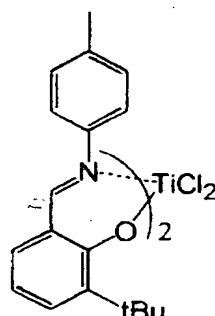
[0198]



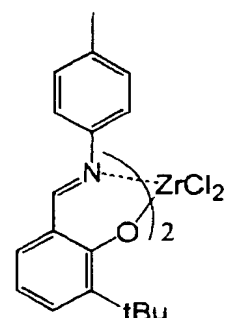
Compound 13



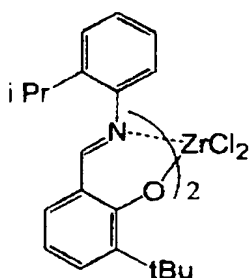
Compound 14



Compound 15



Compound 16



Compound 17

[0199]

[Example 1]

To a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was introduced, and the liquid phase and the gas phase were saturated with ethylene. Thereafter, 1.1875 mmol (in terms of aluminum atom) of methylaluminoxane (MAO) was added, and successively 0.00475 mmol of the titanium compound (A-1) obtained in the Synthesis Example 1 was added to initiate polymerization. The reaction was conducted at 25 °C for 30 minutes in an ethylene gas atmosphere at normal pressure, and then a small amount of isobutanol was added to terminate the polymerization. After the polymerization was

completed, the reaction product was introduced into a large amount of methanol to precipitate a polymer in the whole amount. Then, hydrochloric acid was added, and filtration was effected using a glass filter. The resulting polymer was vacuum dried
5 at 80 °C for 10 hours to obtain 8.02 g of polyethylene (PE).

[0200]

The polymerization activity per 1 mmol of titanium was 3,400 g, and the intrinsic viscosity $[\eta]$ of the polyethylene was 8.44 dl/g.

10 [0201]

[Example 2]

To a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was introduced, and the liquid phase and the gas phase were saturated with 100 l/hr of ethylene.
15 Thereafter, 1.25 mmol (in terms of aluminum atom) of methylaluminoxane and 0.005 mmol of the compound 1 were added to initiate polymerization. The polymerization was conducted at 50 °C for 10 minutes, and then a small amount of isobutanol was added to terminate the polymerization.

20 [0202]

The polymer suspension obtained was introduced into 1.5 liters of methanol containing a small amount of hydrochloric acid to precipitate a polymer. Then, filtration was effected using a glass filter to remove the solvent. The resulting

polymer was washed with methanol and vacuum dried at 80 °C for 10 hours, to obtain 3.30 g of polyethylene. The polymerization activity was 3,960 g/mmol-Ti·hr, and the intrinsic viscosity $[\eta]$ of the polyethylene was 6.37 dl/g.

5 [0203]

[Example 3]

Polymerization was carried out in the same manner as in Example 2, except that the polymerization temperature was varied to 75 °C. The results are shown in Table 1.

10 [0204]

[Example 4]

To a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was introduced, and the liquid phase and the gas phase were saturated with 100 l/hr of ethylene. Thereafter, 0.25 mmol of triisobutylaluminum (TIBA) was added, and successively 0.005 mmol of the compound 1 and 0.006 mmol of triphenylcarbeniumtetrakis(pentafluorophenyl)borate (Ph₃CBPh₃*) were added to initiate polymerization.

[0205]

20 The reaction was conducted at 25 °C for 1 hour in an ethylene gas atmosphere at normal pressure. After the polymerization was completed, the reaction product was introduced into a large amount of methanol to precipitate a polymer in the whole amount. Then, hydrochloric acid was added,

and filtration was effected using a glass filter. The resulting polymer was vacuum dried at 80 °C for 10 hours, to obtain 0.50 g of polyethylene (PE).

[0206]

5 The polymerization activity per 1 mmol of titanium was 100 g, and the intrinsic viscosity $[\eta]$ of the polyethylene was 10.6 dl/g.

[0207]

[Example 5]

10 To a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was introduced, and the liquid phase and the gas phase were saturated with 100 l/hr of ethylene. Thereafter, 0.25 mmol of triisobutylaluminum, 0.005 mmol of the compound 1 and 0.006 mmol of triphenylcarbeniumtetrakis
15 (pentafluorophenyl)borate were added to initiate polymerization. The polymerization was conducted at 75 °C for 30 minutes, and then a small amount of isobutanol was added to terminate the polymerization.

[0208]

20 The polymer suspension obtained was introduced into 1.5 liters of methanol containing a small amount of hydrochloric acid to precipitate a polymer. Then, filtration was effected using a glass filter to remove the solvent. The resulting polymer was washed with methanol and vacuum dried at 80 °C for

10 hours, to obtain 0.71 g of polyethylene. The polymerization activity was 280 g/mmol-Ti·hr, and the intrinsic viscosity $[\eta]$ of the polyethylene was 7.22 dl/g.

[0209]

5 The above-mentioned results are shown in table 1.

[0210]

Table 1

Examples of ethylene polymerization at normal pressure

Ex.	Compound	Amount (mmol)	Cocatalyst	Amount (mmol)	Temp. (°C)	Time (min)	Yield (g)	Activity (g/mmol-M·h)	$[\eta]$ (dl/g)
1	1	0.00475	MAO	1.1875	25	30	8.02	3400	8.44
2	1	0.005	MAO	1.25	50	10	3.30	3960	6.37
3	1	0.005	MAO	1.25	75	10	3.14	3770	5.48
4	1	0.005	TIBA/Ph ₃ CBPh ₃ *	0.25/0.006	25	60	0.50	100	10.6
5	1	0.005	TIBA/Ph ₃ CBPh ₃ *	0.25/0.006	75	30	0.71	280	7.22

[0211]

15 [Example 6]

To a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was introduced, and the liquid phase and the gas phase were saturated with ethylene. Thereafter, 2.5 mmol (in terms of aluminum atom) of methylaluminumoxane was added, and successively 0.005 mmol of the zirconium compound (compound 2) was added to initiate polymerization. The reaction was conducted at 25 °C for 5 minutes in an ethylene gas atmosphere at normal pressure. After the polymerization was completed, the reaction product was introduced into a large

amount of methanol to precipitate a polymer in the whole amount. Then, hydrochloric acid was added, and filtration was effected using a glass filter. The resulting polymer was vacuum dried at 80 °C for 10 hours, to obtain 6.10 g of polyethylene (PE).

5 [0212]

The polymerization activity per 1 mmol of zirconium was 14,600 g, and the intrinsic viscosity $[\eta]$ of the polyethylene was 0.30 dl/g.

[0213]

10 [Example 7 - 23]

Polymerization was carried out in the same manner as in Example 6, except that the compound 2 was used and the polymerization conditions were varied to those shown in Table 2. The results are shown in Table 2.

15 [0214]

Table 2

Ex.	Com- pound	Amount (mmol)	Cocatalyst	Temp. (°C)	Time (min)	Yield (g)	Activity (g/mmol-M·h)	[η] (dl/g)
6	2	0.005	MAO(2.5)	25	5	6.10	14.6	0.30
7	↑	0.0005	MAO(0.5)	↑	5	4.85	116.4	0.31
8	↑	0.0002	↑	↑	5	3.29	197.4	0.32
9	↑	0.0001	↑	↑	5	2.72	326.4	0.21
10	↑	0.00002	MAO(1.25)	↑	5	0.77	462.0	0.28
11	↑	0.00002	↑	40	5	0.90	540.0	0.33
12	2	0.0002	MAO(1.25)	0	5	3.09	185.4	0.27
13	↑	0.0002	↑	10	5	3.64	218.4	0.29
14	↑	0.0002	↑	30	5	3.70	222.0	0.26
15	↑	0.0002	↑	40	5	4.21	252.6	0.33
16	↑	0.0002	↑	50	5	2.95	177.0	0.30
17	↑	0.0002	↑	60	5	2.99	179.4	0.39
18	↑	0.0002	↑	70	5	2.11	126.6	0.41
19	2	0.00008	MAO(1.25)	25	5	2.67	400.5	0.28
20	↑	0.00008	↑	25	15	7.58	379.0	0.30
21	↑	0.00008	↑	25	30	12.42	310.5	0.31
22	↑	0.0002	↑	50	15	5.89	117.8	0.60
23	↑	0.0002	↑	50	30	9.67	96.7	1.23

[0215]

15 [Example 24]

To a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was introduced, and the liquid phase and the gas phase were saturated with ethylene. Thereafter, 0.25 mmol of triisobutylaluminum (TIBA) was added, and successively 0.0005 mmol of the zirconium compound (compound 2) and 0.001 mmol of triphenylcarbeniumtetrakis(pentafluorophenyl)borate (TrB) were added to initiate polymerization. The reaction was conducted at 25 °C for 10 minutes in an ethylene gas atmosphere at normal pressure. After the polymerization

was completed, the reaction product was introduced into a large amount of methanol to precipitate a polymer in the whole amount. Then, hydrochloric acid was added, and filtration was effected using a glass filter. The resulting polymer was vacuum dried
 5 at 80 °C for 10 hours, to obtain 0.34 g of polyethylene (PE).
 [0216]

The polymerization activity per 1 mmol of zirconium was 4,080 g, and the intrinsic viscosity $[\eta]$ of the polyethylene was 12.6 dl/g.

10 [0217]

[Example 25 - 29]

Ethylene polymerization was carried out in the same manner as in Example 24, except that the compound 2 was used and the polymerization conditions were varied to those shown in Table 3.

15 [0218]

The above-mentioned results are shown in Table 3.

[0219]

Table 3

Ex.	Compound	Amount (mmol)	Cocatalyst	Temp. (°C)	Time (min)	Yield (g)	Activity (g/mmol-M·h)	$[\eta]$ (dl/g)
24	2	0.0005	TrB/TIBA(0.01/0.25)	25	10	0.34	4.08	12.6
25	↑	0.001	TrB/TIBA(0.02/0.25)	25	10	0.31	1.86	15.0
26	↑	0.0025	TrB/TIBA(0.05/0.25)	25	10	1.28	3.07	14.8
27	↑	0.0005	TrB/TIBA(0.01/0.25)	25	10	0.27	3.24	20.1
28	↑	0.0005	TrB/TIBA(0.01/0.25)	50	10	0.22	2.64	21.1
29	↑	0.0005	TrB/TIBA(0.01/0.25)	75	10	0.12	1.44	16.3

[0220]

[Example 30 - 50]

Ethylene polymerization was carried out in the same manner as in Example 1, except that the compounds 3 to 17 were used and the polymerization conditions were varied to those shown in Table 4. The results are shown in Table 4.

[0221]

Table 4

Examples of ethylene polymerization at normal pressure

Ex.	Compound	Amount (mmol)	Cocatalyst	Amount (mmol)	Temp. (°C)	Time (min)	Yield (g)	Activity (g/mmol-M·h)	[η] (dl/g)
30	3	0.005	MAO	1.25	25	5	2.69	6460	0.75
31	3	0.005	MAO	1.25	75	5	3.47	8330	0.47
32	4	0.005	MAO	1.25	25	30	2.15	860	0.40
33	5	0.005	MAO	1.25	25	30	2.66	1060	8.34
34	6	0.0005	MAO	1.25	25	5	1.38	33100	0.24
35	7	0.005	MAO	1.25	25	5	1.93	4630	6.84
36	8	0.005	TIBA/Ph ₃ CBPh ₃ *	0.25/0.006	25	30	0.17	68	22.60
37	8	0.005	MAO	1.25	25	5	1.72	4130	0.10
38	9	0.0001	MAO	0.5	25	5	1.01	121000	0.21
39	9	0.005	TIBA/Ph ₃ CBPh ₃ *	0.25/0.006	25	30	2.57	1030	14.20
40	10	0.0005	MAO	1.25	25	5	1.22	29300	0.24
41	10	0.005	TIBA/Ph ₃ CBPh ₃ *	0.25/0.006	25	5	2.87	6890	0.30
42	11	0.005	MAO	1.25	25	10	2.05	2460	4.90
43	12	0.005	MAO	1.25	25	10	3.22	3860	0.74
44	13	0.0005	MAO	1.25	25	5	1.68	40300	4.42
45	13	0.005	TIBA/Ph ₃ CBPh ₃ *	0.25/0.006	25	5	2.22	5330	1.87
46	14	0.005	MAO	1.25	25	30	2.34	936	0.31
47	15	0.005	MAO	1.25	25	30	1.04	2500	3.47
48	16	0.005	MAO	1.25	25	5	5.67	13600	0.34
49	17	0.005	MAO	1.25	25	5	5.11	12300	6.34
50	17	0.005	TIBA/Ph ₃ CBPh ₃ *	0.25/0.006	25	5	1.98	4750	5.67

[0222]

[Example 51]

To a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was introduced, and the liquid phase and the gas phase were saturated with a mixed gas of 50 l/hr of ethylene and 150 l/hr of propylene. Thereafter, 1.25 mmol (in terms of aluminum atom) of methylaluminoxane and 0.005 mmol of the compound 1 were added to initiate polymerization. The polymerization was conducted at 25 °C for 15 minutes, and then a small amount of isobutanol was added to terminate the polymerization.

10 [0223]

The polymer suspension obtained was introduced into 1.5 liters of methanol containing a small amount of hydrochloric acid to precipitate a polymer. Then, filtration was effected using a glass filter to remove the solvent. The resulting polymer was washed with methanol and vacuum dried at 80 °C for 10 hours, to obtain 0.95 g of an ethylene/propylene copolymer. The polymerization activity was 760 g/mmol-Ti·hr, the propylene content as measured by IR was 4.67 % by mol, and the intrinsic viscosity $[\eta]$ of the copolymer was 2.21 dl/g.

20 [0224]

[Example 52 - 57]

Copolymerization was carried out in the same manner as in Example 51, except that the compounds shown in table 5 were used and the polymerization time was varied to 10 minutes.

[0225]

The above-mentioned results are shown in table 5.

[0226]

Table 5

5 Examples of ethylene/propylene copolymerization
 at normal pressure

Ex.	Compound	Amount (mmol)	Cocatalyst	Amount (mmol)	Temp. (°C)	Time (min)	Yield (g)	Activity (g/mmol-M·h)	[η] (dl/g)	Propylene content (mol%)
1	1	0.005	MAO	1.25	25	15	0.95	760	2.21	4.67
2	2	0.005	MAO	1.25	25	10	8.42	10100	0.03	29.2
3	3	0.005	MAO	1.25	25	10	2.3	2760	0.32	7.19
4	6	0.005	MAO	1.25	25	10	3.64	4370	0.14	10.2
5	9	0.005	MAO	1.25	25	10	4.15	4980	0.13	12.43
6	10	0.005	MAO	1.25	25	10	3.31	3970	0.13	8.3
7	13	0.005	MAO	1.25	25	10	1.92	2300	3.63	3.09

[0227]

[Example 58]

15 To a 500 ml glass autoclave thoroughly purged with
nitrogen, 250 ml of toluene was introduced. Then, 100 l/hr
of ethylene and 20 l/hr of butadiene were passed through the
system. After 10 minutes, 5.0 mmol (in terms of aluminum atom)
of methylaluminoxane was added, and successively 0.01 mmol of
20 the titanium compound (compound 1) was added to initiate
polymerization. The reaction was conducted at 25 °C for 20
minutes with passing the mixed gas of ethylene and butadiene
at normal pressure, and then a small amount of methanol was
added to terminate the polymerization. The reaction product

was introduced into a large amount of hydrochloric acid/methanol to precipitate a polymer in the whole amount. The polymer was filtered with a glass filter and vacuum dried at 80 °C for 10 hours, to obtain 0.53 g of an ethylene/butadiene
5 copolymer.

[0228]

The polymerization activity per 1 mmol of titanium was 149 g, and the intrinsic viscosity $[\eta]$ of the copolymer was 1.46 dl/g. The content of all the butadiene units in the
10 copolymer, as determined by NMR analysis, was 0.9 % by mol (1,4-cis form + 1,4-trans form: 0.8 % by mol, 1,2-vinyl form: 0.1 % by mol, cyclopentane skeleton: less than 0.1 % by mol (lower than the detection limit)).

[0229]

15 [Example 59]

Polymerization was carried out in the same manner as in Example 58, except that the zirconium compound (compound 2) was used in place of the titanium compound (compound 1) and the polymerization time was varied to 5 minutes. The yield
20 of the copolymer was 2.65 g.

[0230]

The polymerization activity per 1 mmol of zirconium was 3,180 g, and the intrinsic viscosity $[\eta]$ of the copolymer was 0.70 dl/g. The content of all the butadiene units in the

copolymer, as determined by NMR analysis, was 1.2 % by mol (1,4-cis form + 1,4-trans form: 1.1 % by mol, 1,2-vinyl form: 0.1 % by mol, cyclopentane skeleton: less than 0.1 % by mol (lower than the detection limit)).

5 [0231]

[Example 60]

Polymerization was carried out in the same manner as in Example 59, except that the polymerization time was varied to 20 minutes and the flow rates of ethylene and butadiene were
10 varied to 20 l/hr and 80 l/hr, respectively. The yield of the copolymer was 0.74 g.

[0232]

The polymerization activity per 1 mmol of zirconium was 446 g, and the intrinsic viscosity $[\eta]$ of the copolymer was
15 0.87 dl/g. The content of all the butadiene units in the copolymer, as determined by NMR analysis, was 5.3 % by mol (1,4-cis form + 1,4-trans form: 4.7 % by mol, 1,2-vinyl form: 0.6 % by mol, cyclopentane skeleton: less than 0.1 % by mol (lower than the detection limit)).

20 [0233]

[Example 61]

Polymerization was carried out in the same manner as in Example 59, except that the polymerization time was varied to 5 minutes and the flow rates of ethylene and butadiene were

varied to 50 l/hr and 50 l/hr, respectively. The yield of the copolymer was 0.57 g.

[0234]

The polymerization activity per 1 mmol of zirconium was
5 342 g, and the intrinsic viscosity $[\eta]$ of the copolymer was
0.34 dl/g. The content of all the butadiene units in the
copolymer, as determined by NMR analysis, was 2.3 % by mol
(1,4-cis form + 1,4-trans form: 2.3 % by mol, 1,2-vinyl form:
0.1 % by mol, cyclopentane skeleton: less than 0.1 % by mol
10 (lower than the detection limit)).

[0235]

[Example 62]

To a 1-liter SUS autoclave thoroughly purged with
nitrogen, 500 ml of heptane was introduced, and the gas phase
15 and the liquid were saturated with ethylene at 50 °C. Then,
1.25 mmol (in terms of aluminum) of methylaluminoxane and 0.001
mmol of the compound 1 were added, and polymerization was
performed for 15 minutes under an ethylene pressure of 8
kg/cm²-G.

20 [0236]

To the polymer suspension obtained, 1.5 liters of
methanol containing a small amount of hydrochloric acid was
added to precipitate a polymer. Then, filtration was effected
using a glass filter to remove the solvent. The resulting

polymer was washed with methanol and vacuum dried at 80 °C for 10 hours, to obtain 11.22 g of polyethylene. The polymerization activity was 44.9 g/mmol-Ti·hr, and the intrinsic viscosity $[\eta]$ of the polyethylene was 7.91 dl/g.

5 [0237]

[Example 63 - 66]

Polymerization was carried out in the same manner as in Example 62, except that the other compounds as catalysts were used and the polymerization conditions were varied to those
10 shown in Table 6.

[0238]

The above-mentioned results are shown in table 6.

[0239]

Table 6

15 Examples of ethylene polymerization under pressure

Ex.	Compound	Amount (mmol)	Cocatalyst	Amount (mmol)	Temp. (°C)	Time (min)	Yield (g)	Activity (g/mmol-M·h)	$[\eta]$ (dl/g)
62	1	0.001	MAO	1.25	50	15	11.22	44.9	7.91
63	1	0.001	MAO	1.25	75	15	11.96	47.8	7.31
64	2	0.00005	MAO	1.25	50	15	14.90	1192	1.15
65	3	0.00025	MAO	1.25	50	15	8.28	132	2.3
66	7	0.001	MAO	1.25	50	15	4.83	19.3	4.44

20

[0240]

[Example 67]

Preparation of solid catalyst component

In 154 liters of toluene, 10 kg of silica having been

dried at 250 °C for 10 hours was suspended, and the suspension was cooled to 0 °C. Then, 57.5 liters of a methylaluminoxane solution ($\text{Al} = 1.33 \text{ mol/l}$) was dropped over a period of 1 hour. During the addition, the temperature of the system was maintained at 0 °C, and the reaction was conducted at 0 °C for 30 minutes. Then, the temperature of the system was raised up to 95 °C over a period of 1.5 hours, and at this temperature the reaction was conducted for 20 hours. The temperature of the system was then lowered to 60 °C, and the supernatant liquid was removed by decantation. The resulting solid catalyst component was washed twice with toluene and resuspended in toluene, to obtain a solid catalyst component (A) (whole volume: 200 liters).

[0241]

22.4 ml of the suspension of the solid catalyst component (A) as obtained above was transferred into a 200 ml glass flask, and then 175 ml of toluene and 4.8 ml of a toluene solution of the compound 1 ($\text{Ti} = 0.01 \text{ mmol/l}$) were added. The mixture was stirred at room temperature for 2 hours. The resulting suspension was washed three times with 200 ml of hexane, and hexane was added to give 200 ml of a suspension and a solid catalyst component (B).

[0242]

Polymerization

To a 2-liter SUS autoclave thoroughly purged with nitrogen, 1 liter of heptane was introduced, and the gas phase and the liquid were saturated with ethylene at 50 °C. Then, 1.0 mmol of triisobutylaluminum and 0.005 mmol (in terms of
5 Ti atom) of the solid catalyst component (B) were added, and polymerization was performed for 90 minutes under an ethylene pressure of 8 kg/cm²-G.

[0243]

The polymer suspension obtained was filtered with a glass
10 filter, washed twice with 500 ml of hexane and vacuum dried at 80 °C for 10 hours, to obtain 8.96 g of polyethylene. The polymerization activity was 1,790 g/mmol-Ti, and the intrinsic viscosity [η] of the polyethylene was 11.7 dl/g.

[0244]

15 [Example 68]

Polymerization

To a 200 ml reactor thoroughly purged with nitrogen, 60 ml of heptane and 40 ml of 1-hexene were introduced, and they were stirred at 25 °C. Thereafter, 0.25 mmol of triisobutylaluminum
20 was added, and then a mixed solution of 0.1 mmol of triisobutylaluminum, 0.01 mmol of the compound 1 and 0.012 mmol of triphenylcarbeniumtetrakis(pentafluorophenyl)borate was added to initiate polymerization. The reaction was conducted at 25 °C for 1 hour, and then a small amount of isobutanol was

added to terminate the polymerization.

[0245]

The polymer suspension obtained was added little by little to 1 liter of acetone to precipitate a polymer. The polymer was separated from the solvent and vacuum dried at 130 °C for 10 hours, to obtain 3.15 g of polyhexene. The polymerization activity was 315 g/mmol-Ti·hr. The molecular weight (Mw), as measured by GPC, was 1,460,000 (in terms of polystyrene), and the molecular weight distribution (Mw/Mn) was 2.06.

[Brief description of the drawings]

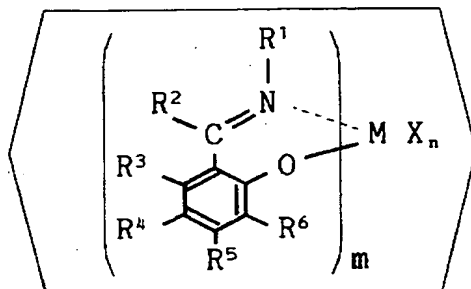
Fig. 1 shows steps for preparing the olefin polymerization catalyst according to the invention.

[Document] Drawing

[Fig.1]

(A) Transition metal component

5



M: transition metal atom of group 3-11 of the periodic table

R¹-R⁶: hydrogen, hydrocarbon group, etc.

m: 1-3

n: 1-3

X: halogen, hydrocarbon group, etc.

(B) Organometal component

Organometallic compound

Olefin

15

Organoaluminum oxy-compound

Compound reacting with transition
metal compound to form ion pair

(C) Third component

20

(Fine particle carrier)

[Document] Abstract

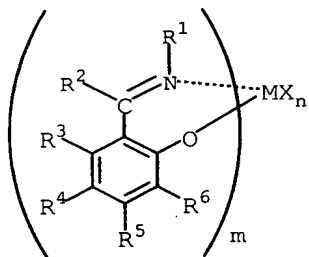
[Summary]

The present invention relates to provide an olefin polymerization catalyst having excellent olefin

5 polymerization activities and a process for preparation of the polymerization an olefin using the catalyst.

The olefin polymerization catalyst comprises (A) a transition metal compound represented by the following formula (I), and (B) an organometallic compound, an organoaluminum oxy-compound or an ionizing ionic compound.

10



M: transition metal of group 3-11 of the periodic table

R¹-R⁶hydrogen atom, hydrocarbon group, etc.

... (I) m: 1-3 n: 1-3

X: halogen atom, hydrocarbon group, etc.

15

[Selected figure] Fig.1

20